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DEPARTMENT OF THE INTERIOR
FRANKLIN K. LANE, SECRETARY
BUREAU OF MINES
VAN. H. MANNING, DIRECTOR

EXTRACTION AND RECOVERY OF RADIUM, URANIUM AND VANADIUM FROM CARNOTITE

BY

CHARLES L. PARSONS, R. B. MOORE, S. C. LIND
AND
O. C. SCHAEFER

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NATIONAL RADIUM INSTITUTE
COOPERATIVE AGREEMENT

JUN 2 1917

[This report has been prepared under a cooperative agreement with the National Radium Institute]

WASHINGTON
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EXTRACTION AND RECOVERY OF RADIUM, URANIUM, AND VANADIUM FROM CARNOTITE.

By Charles L. Parsons, R. B. Moore, S. C. Lind, and
O. C. Schaefer.

CHAPTER I. INTRODUCTION.

Early in 1912, from information received by the Bureau of Mines, it became evident that quantities of valuable radium-bearing ore from Colorado were being exported for manufacture in foreign countries and that at least part of the manufactured product was being returned to this country and sold at a price entirely incommensurate with that received by the miner and the prospector. Consequently, in line with its efforts to increase efficiency in the mining and treatment of mineral resources, the Bureau of Mines undertook an investigation of conditions. Results of this preliminary investigation were published, in the summer of 1913, as Bulletin 70,[a] which gave an outline of the radium deposits of the West, the conditions of mining, the wastes involved, and the status of the production of radium from its ores.

At about this time newspapers and medical journals were publishing statements regarding the value of radium in cancer therapy. These reports, although many of them were exaggerated, brought out clearly the remarkable virtue of the gamma rays for the treatment of cancer and other malignant growths. In view of the fact that the largest known supplies of radium ore in the world are in the States of Colorado and Utah and on the public lands of the United States, it was deemed highly important for the Bureau of Mines to study the production of radium in detail. Such study, it was hoped, would enable the prospector and miner to obtain a fairer price for the ores and would furnish information necessary in case Congress appropriated funds to develop methods for extracting radium from ore on the public lands under Government supervision, to be supplied at cost to the hospitals of the Army, Navy, and Public Health Service.

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[a] Moore, R. B., and Kithil, K. L., A preliminary report on uranium, radium, and vanadium Bull. 70, Bureau of Mines, 1913, 101 pp., 4 pls., 2 figs.

FORMATION OF NATIONAL RADIUM INSTITUTE.

At that time no appropriation for such work was available for this purpose. However, the bureau ascertained that Dr. Howard A. Kelly, of Baltimore, Md., and Dr. James Douglas, of New York City, were deeply interested in the production of radium for use in two hospitals with which they were closely connected. The suggestion was made them that they form a radium institute and endeavor to work up some of the American ores and keep the radium in this country for use among our own people. A member of the bureau went with Dr. Kelly to the Paradox Valley, Colo., and inspected the mines there, it having been agreed that if ore could be procured a radium institute would be founded and necessary funds furnished to work up the ore. As a result of this visit a conference was held with the officers of the Crucible Steel Co., who, through a subsidiary company, control 16 carnotite claims in Montrose County, Colo., which had been held pending the time when extraction of vanadium and uranium from the ore would be profitable. The company agreed that if the National Radium Institute should be formed these claims would be leased to the institute on a 15 per cent royalty basis under an agreement providing for the return of the uranium and vanadium content of the ore to the company. The National Radium Institute was duly incorporated and the claims were leased on the terms mentioned.

COOPERATIVE AGREEMENT BETWEEN THE NATIONAL RADIUM INSTITUTE AND THE BUREAU OF MINES.

Subsequently the institute proposed to the Bureau of Mines that a cooperative agreement looking to the development of the radium ores be made. The legality of the proposed agreement was carefully examined and the agreement was approved by the proper officials, many precedents for similar cooperative work having been found, especially in connection with arrangements between the Department of Agriculture and farmers throughout the country. In the light of the manifestly great usefulness of radium in therapy the importance of studying the ores and their extraction and of disseminating the resulting information was deemed so great and the acceptance of the institute's offer so highly desirable that, on October 13, 1913, the offer was accepted. The text of the agreement follows:

OCTOBER 7, 1913.

The DIRECTOR, BUREAU OF MINES.

SIR: The National Radium Institute (Inc.) is a corporation duly organized and existing under and by virtue of the laws of the State of Delaware, and is interested in the study of the best methods of producing uranium, vanadium, and radium, and in the mining and concentration of ores from which these products may be obtained for use in radium therapy. It is interested in certain carnotite and other suitable ores mined in Colorado from which these products are obtainable.

For the benefit of the people, and to secure the advantage of a scientific and technologic study of efficient methods of production, as well as mining and concentration of the ores, without waste, the institute solicits the cooperation of your bureau, that is, the services, under your supervision, of enough chemists and mineral technologists connected with your bureau as may be necessary for the proper technical control and supervision of the mining and concentration of carnotite and other suitable Colorado ores, in the study of the methods outlined and generally in the prosecution of the investigation contemplated, the results to be published by you.

To aid in such work, the institute will furnish the sum of $150,000, to be available as follows and to be expended, after consultation with us, as you advise: $70,000 during the year ending August 30, 1914; $40,000 during the year ending August 30, 1915; $40,000 during the year ending August 30, 1916, it being estimated that about three years are required for the exhaustive investigation that is desired. The funds received from the sale of any by-products other than radium belong to us, and may also be used in the prosecution of this work. It is proposed to expend this money in the mining of the carnotite or other suitable ores, to an amount of 1,000 tons, more or less, of high-grade ore (over 2 per cent), or in the purchase of such ores as are necessary to an adequate study of the subject, and in the establishment and operation of a plant for the working up of said ores; also in the erection and operation of a small concentration plant for the treatment of any low-grade ore (less than 2 per cent U_3O_8) as may be mined or purchased—and of course in the payment of necessary wages of the plant operatives.

The institute is also entirely willing that any radium produced in excess of 7 grams of anhydrous radium bromide ($RaBr_2$) from any 1,000 tons of carnotite ore may be donated to the bureau for further experiment and study.

As the institute has already on hand 100 tons (more or less) of carnotite, it is made a condition of this offer that this ore be first extracted far enough to demonstrate to the satisfaction of the institute the practicability of the processes employed. Until this is done no more than $5,000 shall be expended on mining or concentration.

At the completion of this demonstration the undersigned may withdraw from this project and shall not thereafter be liable for any further expenditure of money other than sufficient to take up all obligations incurred up to the date of such withdrawal, and no further demands on account of said $150,000 shall be made. All expense incurred in such transaction shall, in any event, be on account of said $150,000.

The institute would esteem it a favor if its cooperation should be recognized on the cover and title page of any published report of the results of this investigation.

If this proposition is acceptable, will you not kindly advise the institute as soon as you conveniently can?

Respectfully,

National Radium Institute (Inc.),
By Howard A. Kelly, *President.*

Washington, D. C., *October 13, 1913.*

The Secretary of the Interior.

Sir: The above letter is respectfully referred to you for your approval.

Very respectfully,

Van. H. Manning,
Acting Director.

Approved October 13, 1913:
Lewis C. Laylin,
Assistant Secretary.

PERSONNEL OF RADIUM PLANT AND INVESTIGATIONS.

Under this agreement, Charles L. Parsons, Chief of the Division of Mineral Technology, was designated by the Director of the Bureau of Mines to take charge of the investigations. He assigned R. B. Moore, physical chemist, to the direct management of the plant subsequently erected at Denver, Colo.; K. L. Kithil, mineral technologist of the bureau, to the management of the mining and concention of the ores; and J. A. Davis, assistant mining engineer, to superintend the mining and concentration work at Long Park, Colo. O. C. Schaefer, who had had experience in chemical-engineering problems and plant construction, was made superintendent of the plant at Denver, and H. M. Eastman, junior chemist in radioactivity, was appointed assistant superintendent. To Mr. Moore was also assigned S. C. Lind, chemist in radioactivity, who had had long experience in the physical chemistry of radium, both at the laboratory of Mme. Curie, in Paris, and in the Radium Research Institute, Vienna. C. F. Whittemore, assistant chemist in radioactivity, and Messrs. J. C. Morgan, Alan Leighton, and H. A. Doerner, junior chemists in radioactivity, have rendered valuable assistance during the progress of the work, as did Prof. Herman Schlundt, who was employed during the summer of 1914 on radium measurements. The experimental work and the installation of apparatus for the electric-furnace production of uranium oxide were done by H. W. Gillett, alloy chemist, and J. M. Lohr, assistant alloy chemist. G. E. Bost, H. H. Barker, and J. E. Underwood, specialists in crystallizing radium, have been added more recently to the force. Each and all of the persons mentioned have loyally and efficiently served the bureau, and hearty acknowledgment of their work is made.

CONSTRUCTION OF PLANT.

Immediately after the signing of the agreement and the organization of the work, plans were begun for constructing a plant at Denver, and for mining the ore at Long Park, some 20 miles from Naturita, Colo. The plant was first built on an experimental basis, and after preliminary operation in the months of March, April, and May, 1914, began regular production of radium in June, 1914. The work was so successful that the directors of the National Radium Institute deemed it advisable to increase the capacity of the plant more than 100 per cent, and the construction of an addition was completed February 1, 1915. In addition, a grinding and sampling mill were built, as was a nitric acid plant, it having been found that a large part of the nitric acid could be recovered as sodium nitrate and used over and over again. The nitric acid plant has been in successful and continuous operation since February 1 of the present year and has greatly reduced the cost of producing radium salts.

The capacity of the plant is 3½ tons of ore per day, and the plant operations have been eminently successful. Up to October 10, 1915, nearly 5 grams of radium element had been extracted and approximately 2½ grams of element delivered in the form of radium bromide of such degree of purity as was desired by the hospitals concerned.

DEVELOPMENT OF EXTRACTION METHODS.

Entirely new methods, differing from former methods not only in detail but in apparatus used, have been devised for extracting radium from the ore, and for converting the sulphates to chlorides. The time required for the cycle of operation is probably much shorter than in any other plant and the recovery of radium is greater. Furthermore, it is believed that the costs of production are less than those of any other method used heretofore. It should be remembered that the methods apply solely to the treatment of carnotite ore. The bureau has been anxious to try to extract radium from pitchblende, the treatment of which would undoubtedly require some modification of the methods used for carnotite. Unfortunately, however, no pitchblende has been available, and it has been impossible to procure even so much as a ton of this material for experimental use. On the other hand, by the time this report has been issued nearly 1,000 tons of carnotite will have been treated.

Incidentally the methods for preparing sodium uranate, uranium oxide, and iron vanadate have been studied, and the necessary principles for procuring these in pure and marketable condition have been evolved. With ore obtained from Government land or produced at a cost as low as that maintained in the operations of the bureau, it has been shown that the cost of producing radium need not exceed $40,000 per gram and that the extraction of at least 90 per cent of the radium present may be obtained from good quality ore, such as the bureau has been able to procure. Full details of these methods, with a description of the plant, apparatus, and chemical-engineering problems involved, appear in the following pages.

A separate report on the mining and concentration of radium ores is being prepared and will shortly be published by the bureau.

In this general summary there are three points on which it is felt that the position of the Bureau of Mines should be made clear—first, the application of radium to the cure of cancer; second, the market or selling price of radium; and third, the object of the bureau in undertaking this investigation.

USE OF RADIUM IN CANCER THERAPY.

The application of radium to the treatment of cancer and other malignant growths has made much more rapid progress in the past two years than is generally appreciated even by the medical profession. All kinds of opinions may be easily had from the laity and from cancer experts, and the public can draw almost any conclusion from the statements appearing in newspapers, but preference should be given the opinions of those persons who have had extended experience in the use of radium and in sufficient quantities to entitle them to speak authoritatively. One thing regarding radium therapy that has been developed during the past two years is that if the gamma rays of radium are to be successfully applied to the cure of cancer a much larger quantity of radium must be used than is possessed by not more than two or three individual surgeons or hospitals in the United States. The bureau knows of no individual or hospital that has had the privilege of working with so much as half a gram of radium that does not report cures in increasing number or that is not able to treat even advanced cases with increasing assurance of success as a knowledge of technique is developed. Also, the extent and variety of the cures reported and the helpful effect of the gamma rays at depth are almost in direct proportion to the quantity of radium that can be applied at one time to the patient. Blacksmiths working with hand forges would have as much right to condemn the smelting of iron in 500-ton blast furnaces as physicians or surgeons working with a few milligrams of radium to condemn its application in quantities of 500 milligrams or more. This statement does not mean that radium in comparatively small amounts may not be effective with some forms of cancer or some malignant growths in their incipiency, but in two American hospitals that have 500 or more milligrams of radium results are being obtained daily that unquestionably will not be duplicated elsewhere until equal quantities are available.

MARKET PRICE OF RADIUM.

The market price of radium for some two or three years has been $120,000 and up per gram of element according to purity. At the time of the beginning of the European war there was 16 to 20 grams of radium contracted for abroad, chiefly in Germany, at prices above $120.000 per gram. Seemingly the war has not affected the market price but simply the amount produced. As to the selling price of radium in the future, the bureau makes no prediction, but it does not follow that the selling price will decline because of the development of cheaper methods of production. Rather is the case somewhat analogous to the production of gold, diamonds, or any other material that is in steady demand but occur only in very small quantities. Beyond doubt, the amount of radium in nature is exceedingly small. Other deposits of radium ores may be found, but it is highly improbable that the rarity of uranium ores will ever be greatly modified, so that the price of the finished material will largely depend on the ability to procure the raw material.

According to the best evidence that the bureau can obtain, and it has investigated the matter carefully, there is not sufficient ore available to maintain for many more years even the rate of production of 1914. In this connection it should be remembered that the radium produced by the National Radium Institute is not for sale nor for distribution. The Radium Institute was organized for the purpose of studying the curative properties of radium and not for private gain. The radium produced is being used in two hospitals—the Howard A. Kelly Hospital in Baltimore and the General Memorial Hospital in New York.

OBJECT OF INVESTIGATIONS.

In undertaking the radium investigations the bureau had two objects in view—first, to enable the miner and prospector to obtain a just return for the ores and, second, to convince the people that radium ores on the public lands of the United States should be mined and treated under Government supervision and the radium placed in the hospitals of the Army, Navy, and Public Health Service for the benefit of the people of this country.

At the time the bureau began its radium investigations, the miners and prospectors were receiving approximately only $75 to $80 per ton for ore containing 2 per cent uranium oxide, this price being for ore delivered f. o. b. New York in transit to Europe. The ore was being sent abroad in quantity and was not being treated in this country, although one or two companies were rapidly purchasing from prospectors available claims at $50 to $200 per claim, and thereby laying the foundation of a future possible monopoly in this rare material. It was hoped that methods could be found that would enable miners or associations of miners to extract the radium from their own ores, place it on the market, and obtain profits that had been going to foreign manufacturers. By August, 1914, when the European war came on, ore was selling for a much higher price than had been obtained in the summer of 1912.

The methods of extracting the radium that have been evolved and are described herein may be utilized under intelligent technical control by any firm, association, or corporation that can obtain the raw material either by purchase or from its own claims. These methods are being patented for the benefit of the people, and may be freely used by anyone within the United States.

It was also the desire of the bureau to show beyond doubt that, if authorized by Congress, the radium could be procured from ores now owned by the people at a cost approximating one-third the market price, and that it was much better policy for the Government to obtain the radium so greatly needed in the hospitals of the Army, Navy, and Public Health Service at a cost not exceeding one-third the present market price than to give these ores to large corporations and then purchase as radium salts material that had belonged to the people, at a price insuring large profits to the possessors.

Unfortunately the bill introduced into Congress in January, 1914, that would have accomplished this purpose failed to pass, and in the meantime the carnotite areas have been thoroughly prospected and the most valuable claims located. Accordingly the bureau must be content with the good that may come to the American people through the radium being extracted in the plant of the National Radium Institute until such time as the Government may furnish funds sufficient to enable it to purchase in the open market such ore as may be necessary to supplement the little that remains unlocated on Government land.

CHAPTER II. DIFFERENT METHODS OF TREATING RADIUM ORES, INCLUDING NITRIC ACID METHOD.

Until a year or two ago little had been published on methods of treating any of the uranium ores for the extraction of radium, although a number of patents have been issued both in this country and abroad. Therefore persons interested in methods of extracting radium have had little to guide them, as details of the methods in use have been closely guarded. The effect has been rather to discourage those who might have been inclined to invest money in the production and sale of radium. Consequently, there is a real need of the presentation of all of the necessary details in the successful treatment of uranium ores, and the refining of the finished products.

The different methods heretofore used may be classified under three general heads, as follows: (1) Use of an acid leach; (2) use of an alkaline leach followed by an acid leach; (3) fusing the ore with some material that will break up the ore and make the extraction of the valuable contents possible. These different methods have been discussed at some length in Bulletin 70,[a] but are described here in more detail.

USE OF ACID LEACH.

In the method involving the use of an acid leach, the two acids employed up to the present are sulphuric and hydrochloric.

LEACHING WITH SULPHURIC ACID.

A number of patents have been issued in connection with the use of sulphuric acid. The Fleck, Haldane, and White patent [b] claims that radium, uranium, and vanadium can be extracted successfully in the following way:

METHOD OF FLECK, HALDANE, AND WHITE.

The ore is crushed, preferably to 20 to 40 mesh, by any suitable means, and is agitated with hot sulphuric acid of 15 to 20 per cent concentration, the proportion of acid used depending upon the quality of the ore. As a rule, 400 pounds of 65° B. sulphuric acid diluted to 15 to 20 per cent is sufficient for the treatment of 1 ton of ore. The resulting acid solution contains the uranium, vanadium, and copper, if copper is present, and is preferably filtered or otherwise clarified. The resulting clear, acid solution is then brought into contact with fresh ore, heated, and agitated, the solution being thereby neutralized. At the same time, a part of the uranium, vanadium, and iron is precipitated on the ore as basic sulphates or carbonates, the effect of this precipitation being to enrich the ore, which may be of low grade. If necessary, the neutral solution is again clarified, and constitutes a part of the stock solution suitable for further treatment. The enriched ore that has served for the neutralization of the acid solution, either alone or mixed with fresh ore, is treated with sulphuric acid, as described above, yielding an acid solution, which, after neutralization, is added to the stock solution.

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[a] Moore, R. B., and Kithil, K. L., A preliminary report on uranium, radium, and vanadium: Bull. 70, Bureau of Mines, 1914, pp. 69–82.

[b] United States patent 890584.

The ore residues from the treatment with sulphuric acid, as well as the residues from the similar treatment of the enriched ore, are freed from remaining values by being washed with dilute sulphuric acid. The resulting acid washings are then strengthened by the addition of sulphuric acid until they contain, preferably 15 to 20 per cent of the acid, and are utilized for continuing the process.

The nearly neutral stock solution, containing uranium, vanadium, iron, and possibly copper, is then treated with sulphurous acid by subjecting the solution to the action of sulphur dioxide obtained by roasting sulphur or sulphide ores. This treatment reduces the iron and the vanadium. Reduction of the iron to the ferrous state is an advantage, because in the subsequent precipitation of the uranium and vanadium less iron is precipitated, and the valuable metals are therefore in a more concentrated form. The sulphuric acid from the sulphur dioxide is also available for the treatment of additional quantities of ore.

The reduced solution is separated from the ore by filtration or decantation, and is treated with such a quantity of finely pulverized limestone as calculation has shown will bring it to the point at which uranium, vanadium, and copper will just begin to be precipitated, calcium sulphate being formed. The solution is then separated from the calcium sulphate, and sufficient pulverized limestone is added to cause complete precipitation of the uranium and vanadium when the liquid is boiled. The precipitate, which comprises a complex mixture containing basic sulphates and carbonates of uranium and vanadium, compounds of iron, and hydrated calcium sulphate, is at first green, but in air changes rapidly to light green or yellow. This precipitate may be used as the final uranium-bearing product, or it may be further refined or concentrated by any known or suitable method, as the radium, of course, remains with the insoluble residue.

The residue may be agitated with water, and after the larger part of the coarse material has settled, the slimes may be separated and allowed to settle. After the decantation of the clear liquid, the residue, consisting largely of calcium sulphate, barium sulphate, and finely divided silica, constitutes the radium concentrate. From this concentrate the radium may be extracted and refined by any suitable method. By the procedure outlined, it is possible to get a radium concentrate carrying 50 to 100 milligrams of radium per ton of concentrate, the exact proportion depending on the grade of the ore treated.

OTHER METHODS.

The other methods of leaching with sulphuric acid are more or less similar to that of Fleck, Haldane, and White. Some involve a preliminary roasting of the ore before treatment with acid.

McCoy's method [a] involves mixing the ore with either dilute or concentrated sulphuric acid to form a mud, and roasting, at first to a temperature of 100° C. and finally to 300° C. or even higher. When the roasted material is leached with water, the iron, vanadium, and uranium are dissolved, and the radium remains with the insoluble residue from which it can be recovered by any suitable means.

In all such methods of leaching the radium remains with the insoluble residue, and usually some sliming method is used to obtain it in a more concentrated form.

If carnotite is treated with hot concentrated sulphuric acid, the radium, instead of being precipitated, is dissolved. If the solution obtained from this treatment is diluted and allowed to stand, radium and barium are precipitated, more barium chloride being added, if necessary. In order to get a good extraction it is necessary to use two to three times as much acid as ore.

Theoretically, it might be possible to get radium into solution by passing carbon dioxide into water in which carnotite ore is suspended. This method, however, does not give satisfactory results.

LEACHING WITH HYDROCHLORIC ACID.

Hydrochloric acid has been used for leaching in a number of commercial plants. The ore is boiled with hydrochloric acid—at some plants with the strong acid, and at others with weak acid—one part of strong acid to two parts of water. As compared with sulphuric acid, hydrochloric has the advantage of putting the radium into solution at the start. Also, as hydrochloric acid has a reducing action on the vanadium, it acts as a good solvent for that metal as well as for the uranium. If strong acid is used, the radium can be precipitated from the acid solution by partial neutralization either with sodium hydroxide or sodium carbonate, preferably the former, and the addition of sodium sulphate and barium chloride if the ore does not contain sufficient barium. After the separation of the precipitated radium-barium sulphate, the uranium and vanadium can be recovered by any suitable process.

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[a] United States patent 1098282.

USE OF ALKALINE LEACH.

It is probable that some of the early experimental work on extracting radium from carnotite ore involved the boiling of the ore with sodium carbonate, thereby getting rid of most of the uranium and part of the vanadium. The residue, after having been thoroughly washed, was then leached with dilute chemically pure hydrochloric acid in order to extract the carbonates present, of which radium would be one. The Haynes-Engle process [a] for the recovery of uranium and vanadium covered this method, but the patent specifications do not show what is necessary for the final recovery of the radium, as at the time the patent was issued carnotite was mainly valuable for uranium and vanadium and not for radium.

HAYNES-ENGLE PROCESS.

According to the Haynes-Engle patent the ore is first crushed to 12 mesh and is then boiled with a solution of an alkaline carbonate, preferably sodium carbonate or potassium carbonate, until the uranium or vanadium, or both, in the ore is dissolved. The strength of the sodium carbonate solution and the length of time necessary to boil it are determined by the proportion of uranium and vanadium in the ore, and will probably vary considerably. The originators of the process claim, however, that 100 pounds of sodium carbonate per ton of ore for each 1 per cent of uranium and vanadium, or either, present will give good results. The time required for boiling should be about one hour. After the uranium and vanadium, or either, has been dissolved, the clear solution is drained into a separate tank. The uranium is precipitated as sodium uranate by the addition of sodium hydroxide to the solution. This precipitate is removed from the solution, which contains all of the vanadium. From the solution, either with or without neutralization, the vanadium is precipitated as calcium vanadate by the addition of water-slaked lime.

It is claimed that an extraction of 80 per cent of the uranium and 60 to 65 per cent of the vanadium can be obtained by this process.

BLEECKER'S PROCESS.

What was lacking in the Haynes-Engle process has been covered by a patent issued to Warren F. Bleecker.[b] After the ore has been boiled with sodium carbonate, as in the Haynes-Engle process, and washed, the residue is leached with a dilute acid, preferably hydrochloric or nitric. This treatment of the ore dissolves the radium, forming radium-barium chloride, and the solution can be drawn off and stored for any approved treatment to recover the radium. If desired, the ore may be leached once more with acid, 10 per cent sulphuric acid being used, the object being to recover the vanadium not extracted by the first leaching.

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[a] United States patent 808839.

[b] United States patent 1065581.

By Bleecker's method not only is nearly all of the uranium and part of the vanadium recovered but the radium is also obtained in soluble form. As the bulk of the liquid would be too great for direct fractionation, it would be necessary to precipitate the radium and barium salts in solution by adding a sufficient quantity of sulphuric acid or sodium sulphate. By this means, practically all of the radium in solution could be recovered as radium-barium sulphate, which would need further treatment, as described in a subsequent chapter.

Another patent [a] issued to Bleecker covered some modifications of the process outlined. Under the later patent the ore is boiled with a solution of an alkaline hydroxide, and, if desired, an alkaline carbonate may be added to the solution. For example, sodium hydroxide and sodium carbonate may be used, in which event the resulting liquid will be a solution of sodium vanadate, from which the vanadium may be recovered by any approved process. After the sodium hydroxide in the ore has been neutralized with acid, the ore is leached with a solution of alkaline carbonate, the temperature of the solution being kept at about 90° C. This treatment will dissolve the uranium as the soluble sodium uranyl carbonate. The solution can be subsequently treated by any suitable process for the recovery of the uranium. After the ore has been thoroughly washed to free it from soluble carbonates and sulphates, it is leached with an acid other than sulphuric, then washed with water. Eight per cent hydrochloric or nitric acid gives good results. By this method the radium is extracted as the soluble chloride in conjunction with barium, calcium, etc., and can be precipitated from the solution, as already described, by the addition of sulphuric acid or sodium sulphate.

EXTRACTION OF RADIUM BY FUSION METHODS.

FUSION WITH SODIUM SULPHATE.

The first method that was used in connection with the extraction of radium was that of fusing pitchblende ores with sodium sulphate. This method was originally used by the Austrian Government in connection with the treatment of the pitchblende ores from the Government mines at St. Joachimsthal. By this fusion the uranium in the ore is changed to sodium uranate, which can be dissolved from the insoluble residue, after leaching with water, by means of dilute sulphuric acid. The radium remains behind with the residue, and was, before the discovery of radium, discarded.

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[a] United States patent 1068730.

PROCEDURE OF HAITINGER AND ULRICH.

The extraction of the radium from this residue is well described by Haitinger and Ulrich,[a] and, with some minor changes, is probably similar to the method now used by the Austrian Government. The work was done in the laboratory of the Austrian Incandescent Gaslight & Electric Co. Ten thousand kilograms (22,000 pounds) of pitchblende residues was treated, representing about 30,000 kilograms (66,000 pounds) of pitchblende containing 53.4 per cent of $U_3 O_8$. Moisture in the material in the various shipments varied from 10.3 to 18.4 per cent. The moisture was driven off at a temperature of 105° C., the 10,000 kilograms of residue losing 1,340 kilograms in this way. The work took two years, owing to time spent on analyses at the start and to experiments to obtain the best results. The method given was developed as being most suitable to the equipment available. Five thousand kilograms annually could be treated.

The chemical operations involved were, first, the decomposition of the residues; second, the removal of the radium sulphate by precipitation; and third, the solution and concentration of the radium sulphate. The first step consisted of digesting the residue with sodium hydroxide, 100 kilograms being boiled for one day with a solution of 50 kilograms of hydroxide in 200 liters of water. Forty per cent of the alkali was converted to sulphate and to silicate. The solution contained some radium, but the total radium so dissolved from the entire 10,000 kilograms of residue represented the radium equivalent of only 10 kilograms. Therefore this solution was thrown away.

After the boiling the residue was allowed to settle and the liquid was decanted. The residue was washed to remove the greater part of the sulphates, filtering and washing being done in a funnel with a capacity of 100 kilograms and having a lead suction tube 3 meters long. The vessel containing the washed residue was placed on a water bath, and the residue was treated with an equal weight of dilute (1:1) crude hydrochloric acid. After prolonged heating the acid solution was decanted and the residue washed with water. The water was then used to dilute the next part of acid for a new sample.

Crystals of calcium sulphate and lead chloride formed in the acid solution as it cooled. Neither the solution nor the crystals contained an appreciable quantity of radium, but nearly all of the polonium and of the actinium was in the solution. The solution was therefore treated with ammonium hydroxide to precipitate the polonium and actinium. The filtrate was not radioactive and was discarded.

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[a] Haitinger, Ludwig, and Ulrich, Karl, Bericht über die Bearbeitung der Pechblend-Rückstände: K. K. Akad. Wissenschaft., vol. 117, 1908, p. 619.

The residue from the treatment with crude hydrochloric acid was boiled in a solution of sodium carbonate, the carbonate, made by the ammonia process, being free from sulphates. Fifty kilograms of sodium carbonate in 200 liters of water was used for a 100-kilogram sample. By this treatment a large part of the radium sulphate was converted to radium carbonate. Therefore, in subsequent treatments the solutions had to be kept free from sulphate. The residue was washed till free from all trace of sulphate and then treated with pure hydrochloric acid. The boiling with soda and the treatment with acid was repeated three times. After the third treatment only 2 per cent of the original radium content remained in the residue, which was thrown away. The soda extracts were practically free from radium. The washing of each of the various residues consumed four to six weeks. The hydrochloric acid extracts, containing nearly all the radium, were united and the radium was precipitated as a sulphate with sulphuric acid. Besides the radium, the precipitate contained, of course, the alkali earths, including calcium, much lead containing radio-lead, and a small quantity of rare earths containing actinium. The sulphate precipitate, called crude sulphate, represented 0.5 to 2 per cent of the weight of the original residue.

The crude sulphate was reconverted to carbonate by repeated boiling with sodium carbonate solution. All of the sulphate from any one sample could not be converted; therefore, the final residue from the treatments was not thrown away, but added to a new part of crude sulphate. After each carbonate treatment, an extraction with hydrochloric acid was made. The lead chloride formed in the solutions was removed and freed from radium by repeated crystallization in hot water. Sixty kilograms of lead chloride was thus obtained from the entire 10,000 kilograms of residue. It was saved and treated for its content of radio-lead.

The hydrochloric acid solutions from the crude sulphate were freed completely from lead by hydrogen sulphide and were then evaporated to dryness on a steam bath. The calcium chloride in the residue so obtained was dissolved in concentrated hydrochloric acid, in which barium chloride is only slightly soluble and radium chloride is still less soluble. The residue remaining, called crude chloride, consisted of radium and barium chlorides, with some strontium and calcium chlorides and traces of other impurities.

From this point on the concentration was continued by fractional crystallizations from water solutions. Radium chloride, which is the least soluble of the chlorides, accumulated in the crystals, the foreign matter remaining more and more in the mother liquor. The first fraction was, of course, the richest in radium. Two steps in this process were of particular importance—first, the separation of as large a quantity of radium-free barium chloride as was possible; second, the making of a relatively large first fraction. The second step could be satisfactorily attained by temporarily stopping the crystallization of the first series until the crystals of the second series were of sufficient radioactivity to be united with the first.

The crystallizations were all carried out on a steam bath in order to avoid contamination with sulphate, as might have occurred if heating had been done with a direct flame.

Finally, two portions of crystals were obtained, one of about 2 kilograms, containing nearly all of the radium, and the other of about 11 kilograms, containing little radium.

The 2-kilogram portion was treated as raw material for the production of radium chloride free from barium. After this portion had been crystallized about 30 times, the first fraction of about 9 grams was further crystallized, and the lower fractions were combined into three groups according to their activity. The 9-gram portion was first purified with hydrogen sulphide, which removed traces of lead that probably came from the glassware. Further work was conducted in quartz vessels. The salt was dissolved in dilute hydrochloric acid, warmed, and allowed to crystallize. Four fractions were so obtained.

Atomic-weight determinations were made with three of the fractions, the values obtained being 143.2, 185.2, and 225. The latter represented practically pure radium chloride.

Some of the lower fractions of barium chloride that were poor in radium were converted to the bromide and then fractionated. Only one portion, that which should contain the most radium—that is, the last of the four analagous fractions—was saved. The other portions were reconverted to chloride and added to the main chloride crystallization system. In all, 3 grams of pure dry radium chloride and 0.236 gram of radium bromide were obtained from 10,000 kilograms of original residue.

RADCLIFFE'S METHOD.

Although Haitinger and Ulrich's method is suitable for the treatment of pitchblende, which contains much more uranium oxide than does the average grade of carnotite, as shipped, the method would not be applicable to the latter ore. The same statement applies to the method that has been used by Radcliffe,[a] as the ore that his method is designed to treat is widely different from the carnotite in Colorado and Utah. The actual mineral carrying the uranium that is found in

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[a] United States patent 1049145.

Olary, South Australia, is carnotite, but it is associated with considerable quantities of ilmenite and rare-earth minerals that are not found in American carnotite.

The dry ore is crushed to pass a 20-mesh sieve, and is then concentrated magnetically; the concentrates amount to about 30 per cent of the original ore, and, as they are insoluble in acids, a fusion process is necessary to effect the initial decomposition. In the fusion process the concentrates are mixed with three times their weight of salt cake and fused in a reverberatory furnace. The fused product is crushed to pass an 8-mesh sieve and is put into wooden vats fitted with agitators. Cold water is fed continuously into the vats at the bottom, and an overflow is provided near the top. By suitable adjustments it is possible to separate out on the bottoms of the vats a considerable amount of comparatively coarse material that is almost free from radium and uranium. The turbid liquid overflowing carries in suspension the radium, lead, and barium as sulphates, together with a considerable amount of finely divided silica. In solution are found the uranium, the rare earths, and part of the iron and "acid earths" contained in the ore. The coarse residues are removed daily, rewashed, and discarded.

The overflow from the dissolving vats is pumped to large lead-lined tanks and allowed to stand all night. The "slimes" settle completely in 12 hours and the clear liquid is drawn off daily and treated for the recovery of uranium. The slimes, which constitute when dry approximately 10 per cent of the weight of the concentrates, are collected weekly and treated for the recovery of radium.

The clear solution, containing the uranium and much of the iron and other bases, together with a large amount of sodium salts, is fed into a series of vats containing a measured excess of a mixture of carbonate and bicarbonate of soda. This is heated and agitated by means of steam jets; the iron and most of the other bases are precipitated, and the uranium, together with some of the rare earths, goes into solution. The iron is filtered off and the uranium solution is made barely acid with sulphuric acid and is heated, the carbon dioxide being expelled by a current of air. The uranium is then precipitated by the addition of ammonia. The ammonium uranate thus formed is thickened in conical settling tanks and in a hydroextractor. The pulp is dried and dehydrated in large muffles. The dried product is broken up and washed repeatedly with hot water to remove sodium salts, the final product containing about 75 per cent U_3O_8.

To recover the radium from the insoluble residue or slimes from the settling tank, the residue is mixed with half its dry weight of strong sulphuric acid and the liquid is allowed to stand for several days.

The residue is then washed by decantation and by the use of a vacuum filter. This treatment reduces the bulk considerably, dissolving out large amounts of iron salts and "acid earths." The washed slime, in quantities of about 200 kilograms, is then boiled in large steel boilers with an excess of a 20 per cent solution of sodium carbonate, the solution being replaced once during the boiling. This treatment dissolves a large amount of silica and converts much of the lead, radium, and barium sulphates to carbonates. The slime is then washed until the wash water gives no reaction for sulphates, and is then fed into a warm dilute solution of hydrochloric acid, agitated for a couple of hours, and allowed to settle all night. The clear solution is siphoned off, and lead, barium, and radium precipitated as sulphates. After having been washed once by decantation, the slime is again treated as above described, two treatments being sufficient to extract most of the radium.

The crude sulphate obtained in this manner is fused with carbonate of soda in large graphite pots and the product digested with hot water. The insoluble residue, after most of the metallic lead has been removed, is thoroughly washed and heated with hydrochloric acid, the solution is evaporated to dryness to dehydrate the silica, and the residue is moistened with acid and digested with hot water, the silica being filtered off.

FUSION WITH SODIUM CARBONATE.

Another method of radium extraction, that has been used by at least one company, is that of fusing the ore or carnotite concentrates with sodium carbonate; about three times as much carbonate as ore being used. The mixture is strongly heated in a reverberatory furnace lined with magnesite brick, and the fused mass is run directly into vats, in which it is leached. In this manner the silica is converted into sodium silicate and goes into solution together with the uranium and vanadium. The iron, calcium, barium, radium, etc., remain as the insoluble residue, which is washed in filter presses. This material is then treated with dilute sulphate-free hydrochloric acid, which dissolves the carbonates, and the radium and barium are precipitated by the addition of the requisite amount of sulphuric acid or sodium sulphate. The whole is allowed to settle in settling tanks, and the clear liquid drawn off, the barium-radium sulphates, mixed with a considerable amount of silica and other impurities, being left as a sludge at the bottom of the tank. This is taken off without previous filtration and dried, forming a crude radium-barium sulphate, which is then refined by a special process involving fractionation from neutral solution.

GENERAL DISCUSSION OF PROCESSES DESCRIBED.

As regards these different processes of radium extraction, it can be plainly seen that each has some disadvantages. Any process that involves the use of sulphuric acid as a leaching agent at once puts the radium in an insoluble form. Although a concentration is usually obtained which may run as high as 10 to 1, or even higher, the advantage of such a concentration is more than overcome by the disadvantage of having to treat the radium as an insoluble rather than a soluble product. The sliming method gives a concentrate consisting largely of calcium sulphate mixed with fine silica, the whole carrying a certain proportion of barium and radium sulphates. Owing to the presence of the silica, none of the short methods for recovering the radium from the insoluble sulphate can be used, and it is necessary to boil the material with sodium carbonate and then leach with chemically pure hydrochloric acid.

The labor required is considerable and makes the cost of refining high. The fact that this method of concentration could be used at the mines was used to justify the extra expense, but as it is cheaper to transport ore than sulphuric acid, the argument does not hold. In addition, the uranium and vanadium concentrate is in an undesirable form which must be retreated before final use. Any process that converts the radium in carnotite into an acid insoluble product, when it is already in the ore in a more easily treated condition, is open to serious criticism.

LEACHING WITH HYDROCHLORIC ACID.

Leaching with hydrochloric acid will prove successful with some carnotite ore, provided the acid is pracitically free from sulphuric acid, or contains less than 0.05 per cent of the latter acid, and provided the ore itself is exceedingly low in gypsum and other sulphates. In other words on a selected ore a hydrochloric-acid leach will prove reasonably satisfactory, and an 80 or even a 90 per cent extraction can be obtained under favorable conditions. The preferable concentration is an acid containing about 20 per cent hydrogen chloride, and a weight equal to that of the ore should be used. The filtration must take place while the acid is hot, and, therefore, must be rapid. The residue should be washed with more dilute acid and then with distilled water. Although a satisfactory extraction is frequently obtained, on the other hand the extraction from many ores may be as low as 50 or even 40 per cent, and the method can not, therefore, be considered satisfactory for universal use with carnotite ores.

FUSION WITH SODIUM CARBONATE AND LEACHING WITH ACID.

The treatment with sodium carbonate, followed by an acid leach, does not have the same objections. Indeed, this method can be used efficiently for the extraction of radium, the objections being more of a mechanical than of a chemical nature. When the ore is boiled with sodium carbonate, about 80 per cent of the uranium and possibly 60 per cent of the vanadium goes into solution. A previous roast or the use of oxidizing materials during the leaching is advantageous, if not necessary. The sodium carbonate solution can be separated either by the use of a filter press or by settling and decantation, as the liquor does not readily filter by gravity through ordinary filtering media. The ore thus treated must be thoroughly washed with distilled water, in order to remove as much as possible of the sodium silicate and sodium sulphate formed in the reaction. After this washing it is necessary to use chemically pure hydrochloric acid, or at least an acid absolutely free from sulphates, for the presence of small amounts of iron or other impurities is not injurious.

It is almost impossible to filter the acid solution after treatment with hydrochloric acid, because small quantities of sodium silicate remain with the ore, and the liberated silicic acid clogs any filtering medium that may be used. Experiments by the National Radium Institute showed that great difficulty would be experienced in filtering at this stage either by gravity, by suction, or by pressure. Again, settling and decantation might prove successful, but would involve the use of a large bulk of dilute acid. During the time required for settling, the radium would tend to precipitate, especially in the presence of silica. The process also involves the handling of the ore twice, but the main difficulties are in connection with filtration or the separation of the liquors from the residues.

After the acid solution has been removed, the radium can be reprecipitated as radium barium sulphate by adding to the acid solution the required amount of barium chloride and either sulphuric acid or sodium sulphate. The radium barium sulphate can then be obtained by settling and decanting the clear liquid from the precipitate, and finally removing the precipitate through an earthenware filter.

Whether the patent covering this process contains any new discovery might be questioned. Moreover, the same results can be obtained by using sodium bicarbonate instead of sodium carbonate.

FUSION WITH SODIUM CARBONATE.

The fusion methods used for pitchblende and the Austrian ores do not apply to American carnotite, although they may have some advantages for the particular ore they are designed to treat. The fusion of carnotite with sodium carbonate has some advantages and some serious disadvantages. The main advantage is that it is adapted to carnotite in any form whether it be ore of 20 or 30 mesh or concentrates of more than 200 mesh. In addition the presence of sulphates in the ore is not deleterious, as they are removed at the same time as the sodium silicate. The disadvantages, however, are numerous. In the first place, as a large bulk of sodium carbonate has to be added to the ore considerable material has to be handled. After the fusion 3.5 tons of fused material are handled for 1 ton of ore or concentrates. The uranium and vanadium is in the filtrate from the leached material, and the presence of so much sodium carbonate and sodium silicate makes the cost of the recovery of the uranium and vanadium excessive.

The uranium can be recovered in one or two ways—either by adding sodium hydroxide directly to the filtrate, or by making the filtrate slightly acid with sulphuric acid and then adding sodium hydroxide to the hot liquid. In the first case the amount of sodium hydroxide required to precipitate the uranium in the presence of so much sodium carbonate is large and usually involves the precipitation also of a considerable amount of silica. The result can be more easily accomplished by first making the solution acid, but this involves again the use of a large amount of sulphuric acid. In addition the crude barium sulphates obtained are mixed with a considerable amount of silica, which makes them difficult to treat by ordinary methods.

It is doubtful whether a total recovery of radium of more than 70 per cent has been obtained by this process. This low recovery and the necessarily high costs more than counterbalances the advantages that the method may have.

POSSIBLE NEW METHODS OF RADIUM EXTRACTION.

In the search for a better method than those outlined the main object to be borne in mind is a high extraction and recovery of the radium. The importance of a high recovery of uranium and vanadium has been, to some degree, unduly emphasized; the main object is to obtain the radium.

ADVANTAGES OF USING NITRIC ACID.

For extracting the radium the use of nitric acid possesses many advantages, especially if the initial cost of the nitric acid can be reduced through the recovery of sodium nitrate as a by-product. The cost of the treatment would be very largely increased if 6 to 7 cents per pound of 100 per cent nitric acid had to be paid instead of the lower cost of hydrochloric acid. On the other hand, if, in connection with the nitric acid method, sodium nitrate can be recovered with small loss and nitric acid be once more made from the sodium nitrate a cycle would be obtained that would reduce the cost of the nitric acid to a figure as low as, if not lower than, that for the hydrochloric acid.

In addition, the solvent action of nitric acid on radium sulphate is much greater than that of hydrochloric acid. Radium belongs to the calcium, strontium, and barium group, and, as analysts know, in order to precipitate barium sulphate completely and efficiently free nitric acid must be removed. Consequently, nitric acid has a much greater solvent action on radium even though the latter may be associated in the ore with reasonable quantities of sulphates.

This greater solvent action of nitric acid was the general basis for the method devised by the Bureau of Mines and used in the plant of the National Radium Institute. It has recently been recognized by Plum,[a] who suggests that possibly the best method for treating carnotite is to boil the ore first with sodium carbonate, leach the washed residue with hydrochloric acid, and follow this leaching with nitric acid in order to dissolve the 10 per cent of radium that he was unable to extract with hydrochloric acid. Plum had in mind the extraction of both radium and other radioactive constituents, such as polonium and actinium, but he plainly indicates that nitric acid can dissolve out of carnotite radium that can not be dissolved by hydrochloric acid, even after the ore has received a preliminary leaching with sodium carbonate. This finding was also established in the preliminary cooperative work carried on two years ago which led to the adoption of the nitric acid method.

When the use of nitric acid at the start will give just as high an extraction as the combined use of sodium carbonate, hydrochloric acid, and nitric acid, there is no need to use the three steps unless it is desired to recover the other radioactive constituents in the ore.

By the method he outlined, Plum was able to recover 89.9 per cent of the radium in the ore on a laboratory scale, using 1 kilogram of material; this extraction has been exceeded a number of times on carload lots in the plant of the National Radium Institute by the use of nitric acid alone. As a scientific accomplishment the recovery of the polonium, actinium, and ionium would be strongly advisable, but as these now have little or no commercial value they can not be taken into consideration in a commercial process.

In the nitric-acid process the radium is at once recovered as a high-grade radium barium sulphate, practically free from silica, and easily treated by improved methods. The process is adapted to recovering either the radium by itself, or the radium, uranium, and vanadium, as the radium is obtained first, and from that point all the other products may be discarded without further treatment, if so desired.

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[a] Plum, H. M., The extraction and separation of the radioactive constituents of carnotite: Jour. Am. Chem. Soc., vol. 37, 1915, p. 1797.

The different steps are each completed in one day, the equipment is not expensive, the extraction and recovery are high, and it is believed that the costs are lower than those with any other process for treating carnotite.

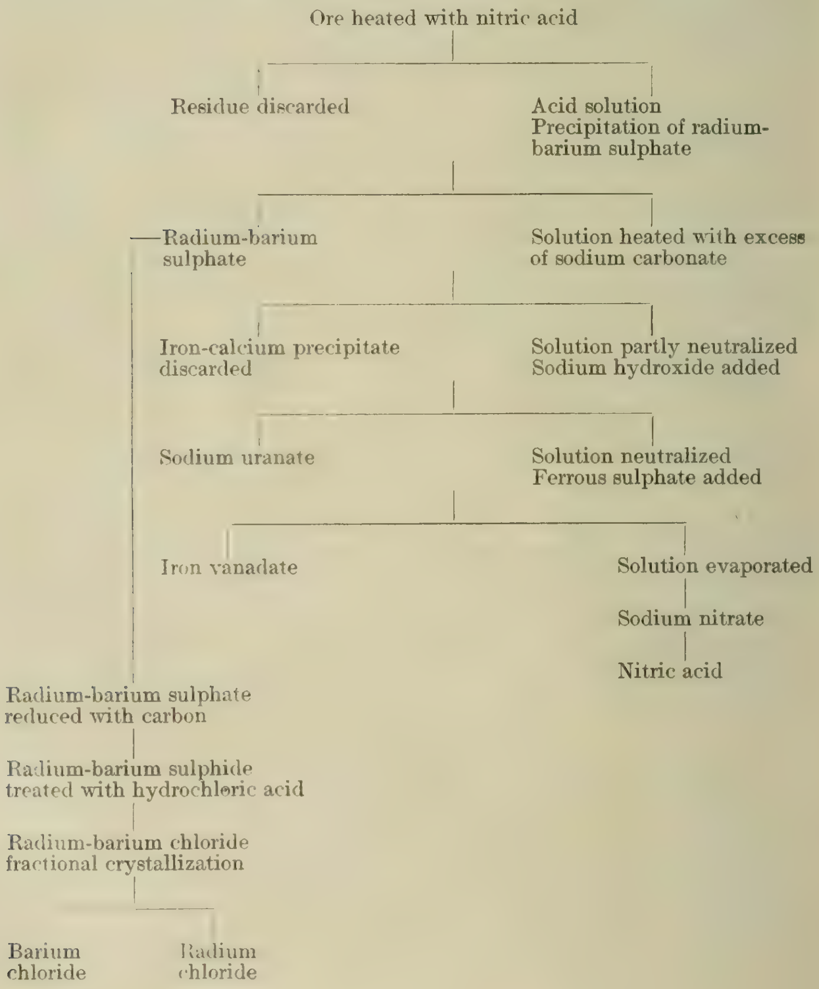
From the data already presented it can be readily seen that each particular type of radium-bearing ore has to receive a more or less different treatment, depending upon the other constituents of the ore. This process has been tried only with American carnotite, and may not be adapted to other radium-bearing ores, as its efficiency in connection with other ores has not yet been fully determined. The process is, however, applicable to the treatment of carnotite ores obtained in Colorado and Utah.

CHAPTER III. BUREAU OF MINES METHOD FOR TREATING CARNOTITE.

OUTLINE OF BUREAU OF MINES METHOD.

The method of treating carnotite ore used by the Bureau of Mines is outlined in this chapter. The process is clearly indicated in the diagram following:

Diagram of steps in Bureau of Mines method of radium extraction.


Ore heated with nitric acid
Residue discarded
Acid solution
Precipitation of radium-barium sulphate
Radium-barium sulphate
Solution heated with excess of sodium carbonate
Iron-calcium precipitate discarded
Solution partly neutralized
Sodium hydroxide added
Sodium uranate
Solution neutralized
Ferrous sulphate added
Iron vanadate
Solution evaporated
Sodium nitrate
Nitric acid
Radium-barium sulphate reduced with carbon
Radium-barium sulphide treated with hydrochloric acid
Radium-barium chloride fractional crystallization
Barium chloride
Radium chloride

LEACHING, FILTERING, AND WASHING ORE.

In the method used by the Bureau of Mines, the ore is ground to 20 mesh and is leached with strong hot nitric acid in acid-proof earthenware pots. The amount of acid used is 121 pounds of 100 per cent nitric acid to 500 pounds of ore, the acid being diluted to 38 per cent strength. However, the strength may be varied somewhat, ores high in sulphates requiring stronger acid. The acid is brought near the boiling point by live steam, which has been passed through a baffle in order to eliminate any impurities from the steam. The ore is then run in, being stirred with a wooden paddle during the process. The acid is heated for 15 minutes longer, with occasional stirring, and the acid is then run into an earthenware vacuum filter, asbestos filter cloths being used. As much as possible of the sand is held back in the pot by means of a long wooden plug manipulated by hand, and this sand is given an acid wash with acid about one-third the strength of that used for the first leaching. This sand is then dumped on the filter, and receives two washings with hot distilled water.

PRECIPITATION.

The whole work from start to finish, leaching, filtering, and washing, can usually be done in about seven hours. The residue is thrown on the dump and the filtrate is run through earthenware pipes into a large precipitating tank made of California redwood, where it is diluted by the addition of water. This solution is stirred, and sodium hydroxide is run in slowly, with the object of reaching as nearly as possible the neutral point without forming a permanent precipitate. If too much alkali is added, both iron and vanadium are precipitated, and contaminate the radium-barium sulphate; on the other hand, if not enough sodium hydroxide is added, the acidity remains too high and the solvent action of the nitric acid on the radium-barium sulphate is not sufficiently decreased. A little practice enables the operator to get the right point by visual observation without titrating, titration not being possible because of the large amount of dissolved material that would be precipitated by an alkali.

A solution of barium chloride is then added, usually in the proportion of about 2 pounds of barium chloride to 1 ton of ore, and after the liquid has been thoroughly stirred, sulphuric acid is slowly added, as stirring continues. Fifteen pounds of sulphuric acid to 1 ton of ore is the preferable quantity. The stirring is continued for one hour, when the whole solution, containing the barium-sulphate precipitate, is elevated to a conical settling tank by means of a centrifugal pump having parts that come in contact with the liquid made of duriron. The solution is then allowed to settle in the conical tank for a few days. In the original plant this period was three days; in the second plant it was increased to four. By means of a floating siphon, the clear solution is decanted into a tank containing an excess of boiling sodium carbonate, where the iron, calcium, and most of the aluminium are precipitated, and the uranium and vanadium go into solution as the double carbonate of uranium and sodium, and as sodium vanadate. The solution must be boiled for at least three hours after all the acid solution has been run in, as otherwise there is considerable loss both in uranium and vanadium, which remain with the iron precipitate.

The radium-barium sulphates and the associated liquor are run onto an earthenware suction filter, filtered, washed, and finally treated with a dilute solution of sodium hydroxide in order to remove the last traces of free acid. The filtrate is run into the carbonate tank with the rest of the acid liquor. The radium-barium sulphates are placed in iron pans and dried in a hot-air oven.

TREATMENT OF SODIUM CARBONATE SOLUTION.

The sodium carbonate solution, carrying the uranium and vanadium, is nearly neutralized with nitric acid, the solution being constantly stirred by means of compressed air; then sodium hydroxide is added to the boiling solution until there is a complete precipitation of sodium uranate. No attempt has been made to control definitely the color of this precipitate, as the sodium uranate has always been converted into oxide for final sale. In addition, the sodium uranate has always carried vanadium, as precipitation of the uranate in the presence of vanadium has so far always caused the precipitate to contain at least 7 or 8 per cent of V_2O_5. Consequently, it is generally necessary to remove the vanadium from the sodium uranate before it can be sold as such. Some early experimental work showed that redissolving with sulphuric acid and reprecipitating with sodium hydroxide would be necessary three or four times before the vanadium could be reduced to less than 1 per cent. This method of refining, therefore, could not be used commercially, and it became necessary to find some other cheaper and more efficient process. Such a process is described in subsequent pages.

TREATMENT OF VANADIUM SOLUTION.

The hot solution from the sodium uranate is completely neutralized with nitric acid, air being blown into the liquid in order to eliminate the carbon dioxide. Ferrous sulphate is then added, the liquid being continually agitated, and the precipitate of iron vanadate is filtered and washed.

The grade of the precipitate depends largely on the final acidity of the solution. If the solution is slightly acid, a high-grade precipitate carrying 40 or 42 per cent V_2O_5 may be obtained. On the other hand, some of the vanadium is not precipitated and is therefore lost. If the solution is perfectly neutral after the addition of the ferrous sulphate, a lower grade product is obtained, carrying 30 to 33 per cent V_2O_5, but all of the vanadium is precipitated. It is advisable not to boil the solution after the addition of the ferrous sulphate, although the solution should be hot at the time of this addition.

TREATMENT OF SODIUM NITRATE SOLUTION.

The filtrate from the iron vanadate is almost wholly a solution of sodium nitrate, the main impurity being a moderate amount of sodium sulphate. The solution is evaporated in iron tanks heated by steam under pressure. Air from a compressor is blown into the solution and evaporation is rapid. As soon as the solution is concentrated enough it is run into steel crystallizing pans where it crystallizes. After draining on draining boards the crystals are collected without further treatment and employed to make fresh nitric acid for use in the plant. As the losses of sodium nitrate are not great, the actual results have been to reduce the cost of the nitric acid below the purchase price of hydrochloric acid of the same acidity.

RECOVERIES MADE BY BUREAU'S PROCESS.

The extraction and recovery of the radium have been excellent even from the start, an extraction of more than 90 per cent having been attained with many carloads of ore. The extraction of the uranium is also practically complete, but a considerable part of the vanadium is left in the ore. In fact, the presence of much vanadium in the ore is a disadvantage, as in the leaching pot the vanadium has a tendency to separate out as vanadic acid, which retards filtration considerably, and tends to reduce the extraction of the radium. Recovery of a few per cent more of the radium content more than compensates for a loss of 50 per cent of the vanadium, and if both can not be recovered, preference must be given the radium. The vanadium in the carnotite goes into solution readily, but roscoelite and other vanadium minerals present are decomposed with much difficulty, and it is not possible on a commercial scale to extract all of the vanadium in the ore, although complete extraction can be attained in the laboratory if enough acid is used.

GENERAL DESCRIPTION OF DENVER PLANT AND EQUIPMENT.

When the plant of the National Radium Institute was projected, it was to be entirely experimental. At the same time, plans were made to build and equip it so that if the experimental work were successful, operation on a commercial basis would be possible by enlarging the plant or by using it as built. Therefore, it was necessary to design, erect, and equip a building that could be used permanently on a commercial scale, and yet to keep the cost down so that if the experimental work were a failure the loss would be as low as possible. For this reason, some equipment was not put into the plant that would have made the original work a little more efficient if the initial investment had been a little larger.

After the experimental work had proved successful, the officials of the National Radium Institute decided that they wished the radium delivered more rapidly than was possible with the original small plant (Pl. I, *A*). Consequently, an additional plant (Pl. I, *B*) was built adjoining the first one. Both were equipped as a separate unit so that they could be run separately or at the same time. For convenience of description, these plants are mentioned in this report as the "first" plant and the "second" plant.

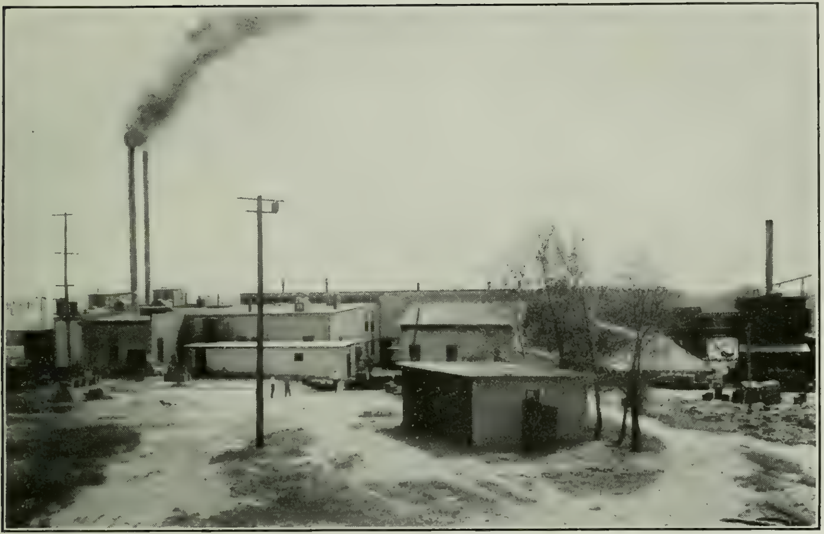
Refining of the radium concentrate is done in a separate building, usually termed the "sulphate building."

During the first six months of work, nitric acid was purchased, but the sodium nitrate was recovered and stored. In December, 1914, and January, 1915, a nitric acid plant was erected, and since then the institute has made its own nitric acid, from the recovered sodium nitrate.

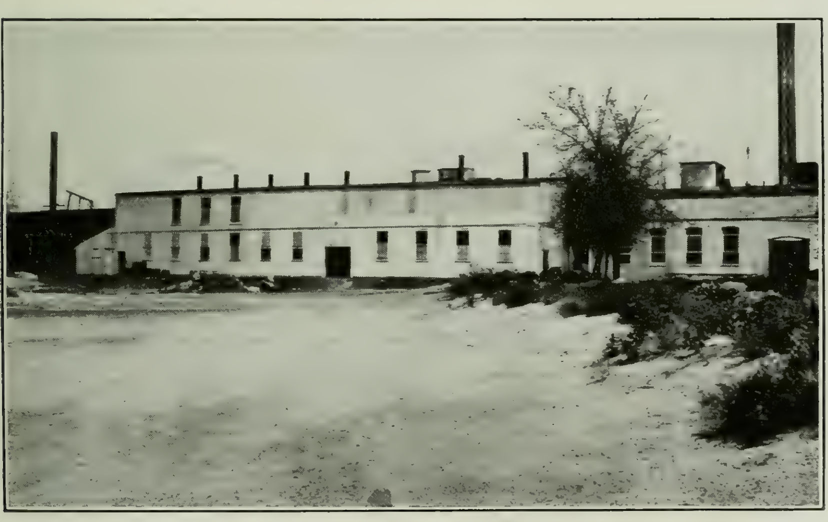
All the buildings of the plant proper are of frame construction, with an outer covering of galvanized iron painted on the inside with one coat of graphite paint to protect it from acid fumes. The roofs of the buildings are of elaterite.

The original or "first" plant (Pl. I, *A*) is 80 feet long, 45 feet wide, 21 feet high on the south, sloping to 18 feet on the north. Adjoining this is a storeroom (shown at extreme left of Plate I, *A*) with doors opening on to a switch that runs past the plant, connecting with both the Denver & Rio Grande and the Colorado & Southern Railroads. The original storeroom was only one story high, but later an additional story was added, as well as a small grinding and sampling plant, which was placed in a room built into one corner of the storeroom.

The "second" plant is 130 feet long, 30 feet wide, and 24 feet high on the north, sloping to 21 feet on the south. The old boiler room was turned into a furnace room for the refining of the uranium, and for the preliminary treatment of the radium-barium sulphates. A new boiler room to serve both plants was erected at the same time as the second plant. It is shown at the right of Plate I, *B;* a plan and sections of this building are shown in Plate II.



A. GENERAL VIEW OF PLANT OF NATIONAL RADIUM INSTITUTE FROM NORTHWEST SHOWING ORIGINAL OR "FIRST" PLANT ADJOINING BRICK BUILDING ON LEFT.



B. VIEW OF PLANT FROM SOUTH, SHOWING NEW OR "SECOND" PLANT.

DESCRIPTION OF FIRST PLANT.

The floor plan of the original or "first" plant is shown in Plate III and the plan of the upper landings on the south side in Plate IV, *A*. The ore and acid are carried to the upper landing by means of the elevator (see Pl. III), the acid being transported in carboys. The handling of the acid in the carboys has been fairly satisfactory, but an improvement could be made by conveying the acid in glass pipe lines to the leaching pots (*27a*, *27b*, etc., Pl. IV, *A*), which would partly eliminate the handling of the acid by hand. This was one of the changes that it was not thought necessary to make under the conditions.

CONSTRUCTION AND OPERATION OF LEACHING POTS.

Each of the earthenware pots in which the leaching is done has a capacity of 107 gallons. Originally each was set in an iron container holding oil that was heated with a steam coil. It was thought that some external method of heating would be necessary in order to quickly raise the temperature of the acid to the desired temperature and to maintain it at this temperature during the period of heating. The results were not satisfactory, as many of the leaching vessels cracked, probably from somewhat uneven heating and the strains to which they were subjected by the packing. During the early stages of the work, in addition to the heating by the oil bath, live steam was run into the acid through glass tubes connected with a pipe leading from a large baffle (*20*, Pls. III and V) that served to eliminate, as much as possible, impurities from the steam. Experience showed that the acid could be heated rapidly enough with live steam alone, and therefore the oil bath was discarded and sand was substituted. The results obtained were an improvement, not so many of the leaching vessels breaking, and the acid being heated at a satisfactory rate. With a view to getting still better results, cement jackets were finally tried, and two or three experimental pots were set in concrete. The results were so good that sand packing has been discarded. The breakage has been small and the cement jackets have proved satisfactory in every way.

The leaching pots are partly covered with wooden covers, each of which has a wooden flue leading to a main flue that goes through the roof (see Pl. IX, *B*, p. 46). A small steam pipe is placed in the main flue so that a jet of steam can be admitted when desired. By this means, practically all of the fumes from the acid can be removed without any trouble. The wooden covers of the pots and the wooden flues are coated with graphite paint, which makes a good protective agent. Stirring is done by hand with wooden paddles (Pl. IX, *B*), as it is almost impossible to install mechanical stirrers that would be satisfactory under the conditions.

During the period of leaching the spouts of the leaching pots are closed with rubber stoppers fastened to cast-iron plates attached by sleeves and set screws to horizontal rods, which are turned by levers inserted through the floor of the upper landing (fig. 1). The stoppers can be removed from the spouts or replaced by means of these levers, which are worked from the upper landing, so that all danger from the splashing of hot acid during the dumping of a pot is eliminated. Such splashing, however, can be reduced to a minimum by inserting a wooden plug at the end of a handle in the upper part of the outlet of the pot before the stopper is removed. When the stopper is taken out and the acid begins to run from the pot, the plug is sucked into the opening. Raising the plug when necessary permits the acid to flow onto the suction filter below at any desired rate.

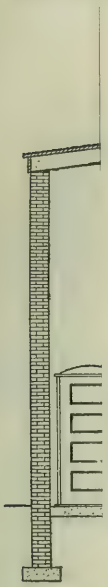
The acid wash is contained in a small wooden tank (*36*, Pl. IV, *B*). From this tank it runs by gravity through an ordinary acid-proof rubber hose to the leaching pots for washing the ore.

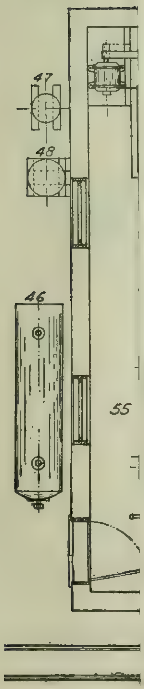
CONSTRUCTION AND OPERATION OF SUCTION FILTERS.

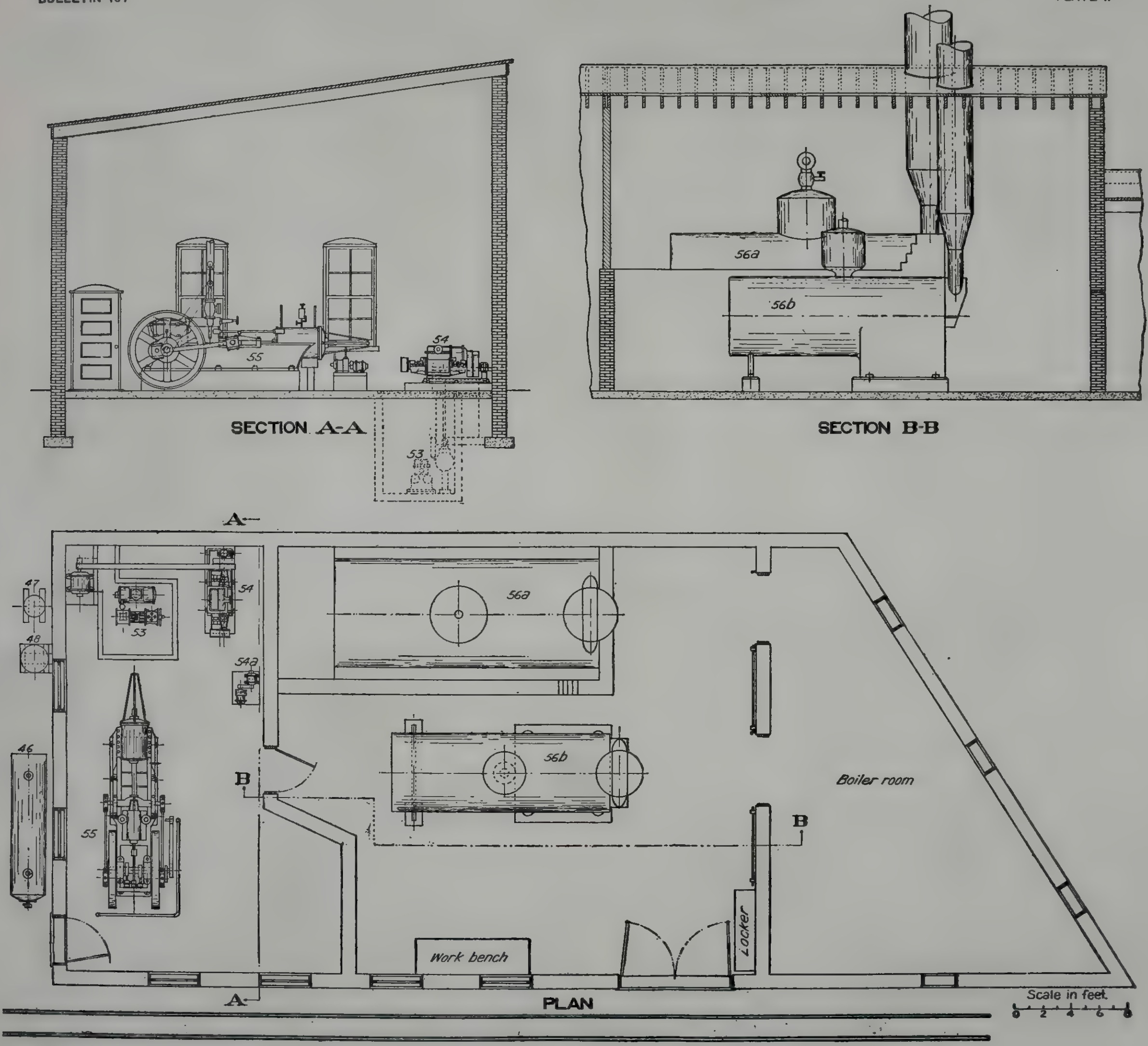
Plate IV, *B*, showing a section of the first plant, indicates the arrangement of the leaching pots (*27a*, *27b*, etc.) and of the suction filters (*28a*, *28b*, etc.) below. These filters were made by the German-American Stoneware Works Co., and are of the "Edda" type (see Pl. IX, *C*, and fig. 1). The upper part of each filter has a capacity of 105½ gallons, as has the lower part. Each bottom vent has a ground-in bibcock, and the upper opening is connected by means of about 6 feet of ½-inch pressure rubber tubing with a pipe running to the vacuum pump. This pipe first connects with a baffle (*47*, Pls. VI and VII), which protects the pump itself. This baffle is filled with vitrified brick, and a strong solution of sodium hydroxide constantly circulates through it.

Each filter is set on a small truck (see Pl. IX, *C*) running on rails so that when the residue is to be removed from the filter the truck can be pushed or pulled from underneath the leaching vessels. The filtering medium consists of an asbestos filter cloth covered with 1 inch of coarse sand over which there are several strips of wood. These strips are held down by three or four bricks suitably placed.

The suction filters have lasted even better than the leaching pots. Before the hot acid is dumped, a small piece of steam hose connected with a steam line is pushed up through the bibcock of each filter so that the lower part is slowly steamed and the temperature raised gradually. Another similar piece of hose, connecting with a second steam line, is pushed down into the upper part of each filter and the






55
54
53
SECTION A-A
56a
56b
SECTION B-B
A
47
48
53
54
54a
56a
46
55
B
56b
Boiler room
B
Locker
Work bench
A
PLAN
Scale in feet
0 2 4 6 8

PLAN AND SECTIONS OF BOILER AND COMPRESSOR PLANT.

46, compressor tank; *53*, pump; *54*, *54a*, rotex vacuum pumps; *55*, compressor; *56a*, *56b*, boilers.

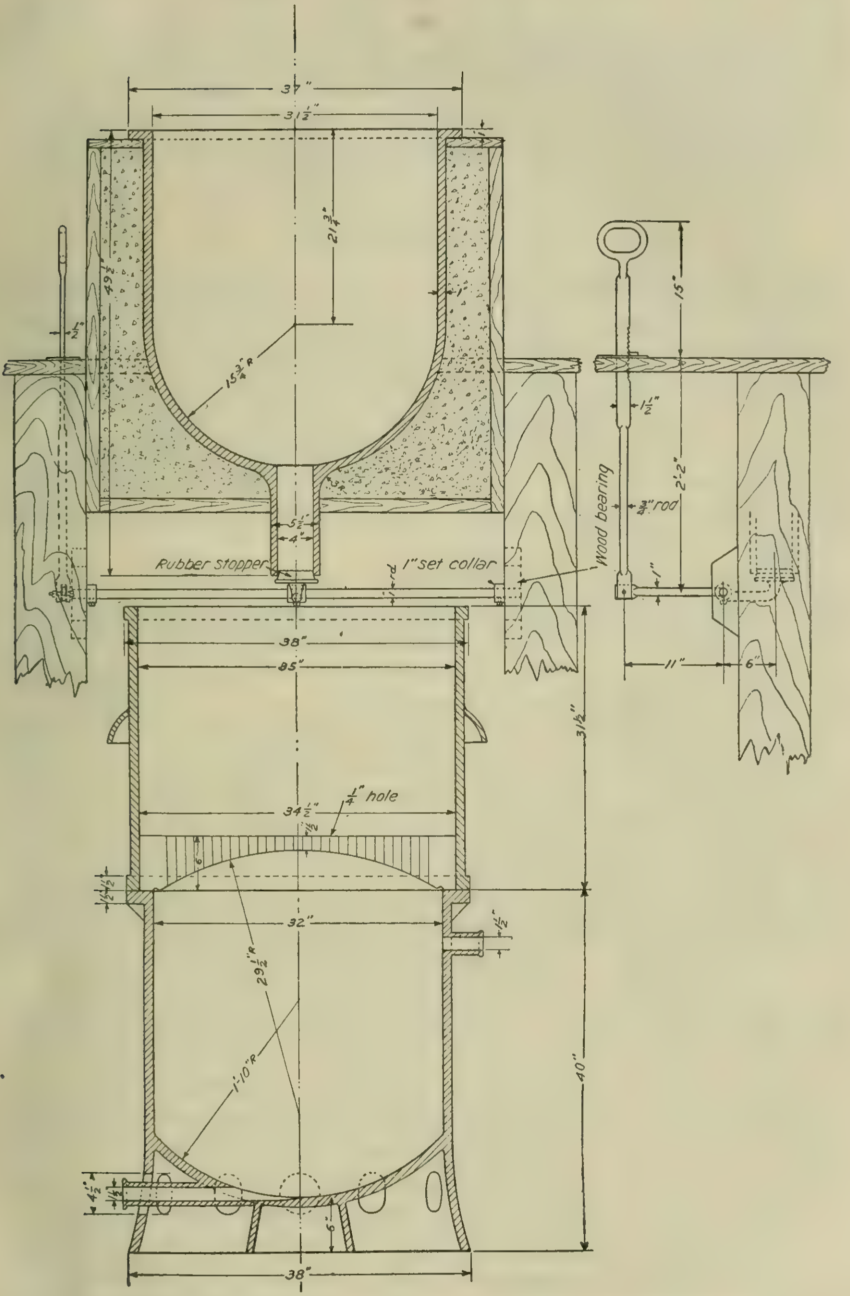

37"
31½"
21¾"
49½"
½"
15¾"R
1"
5½"
4"
Rubber stopper
1" set collar
1" rd
Wood bearing
15"
1½"
2'2"
¾" rod
1"
11"
6"
38"
35"
31½"
¼" hole
34½"
½
6
½
1¼
32"
½"
29½"R
1'10"R
40"
4½"
1½
6"
38"

FIGURE 1.—Sections showing leaching pot, filter, and details of leaching-pot stopper.

whole covered by any suitable material as oilcloth or sacking. In this manner, the upper part of the filter is also steamed and the temperature gradually raised before the hot acid is dumped. With these precautions, few breaks have occurred. The acid from the suction filters flows through a horizontal, acid-proof earthenware line which dips slightly toward the radium precipitating tank, and has an opening below the bibcock of each suction filter.

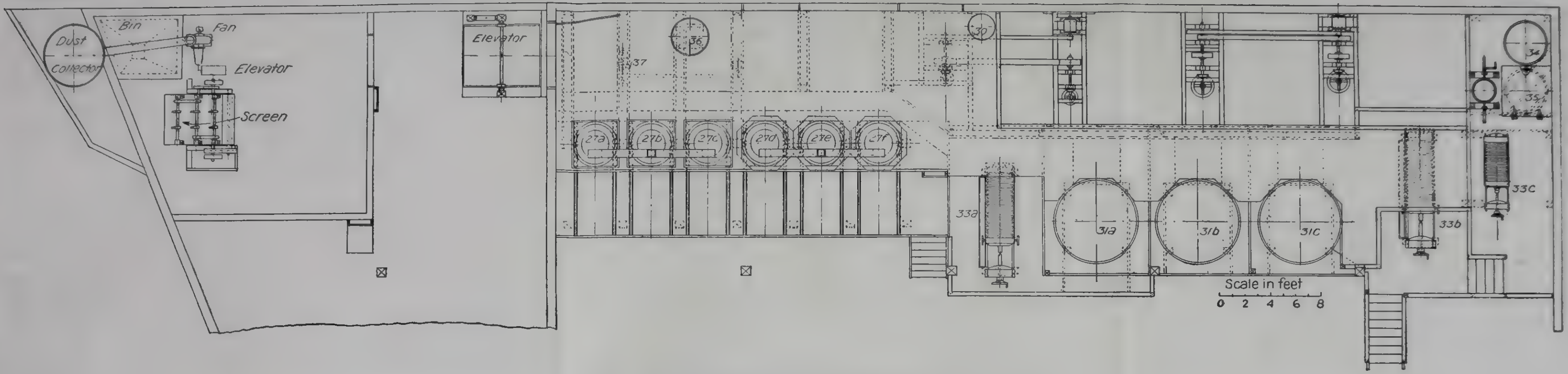
PRECIPITATING TANKS.

The precipitating tanks (Pls. III and VII) are all of 2-inch California redwood, which has satisfactorily withstood the action of acids and of weak alkalies. The radium precipitating tank in the first plant, at the time of writing (September, 1915) has been in use 15 months, and is still in fair condition, although it has been subjected daily to the action of warm dilute nitric acid. Those tanks in which solutions are boiled have a wooden cover, with a wooden flue 12 inches square that extends up through the roof, so that little steam escapes within the plant.

The bottom part of each settling tank is conical, although the vertical staves, which constitute the outside of the tanks, extend the entire length. In other words, these tanks are ordinary 8½ by 5 redwood tanks with a cone inserted in the bottom, and can be supported from below instead of being suspended.

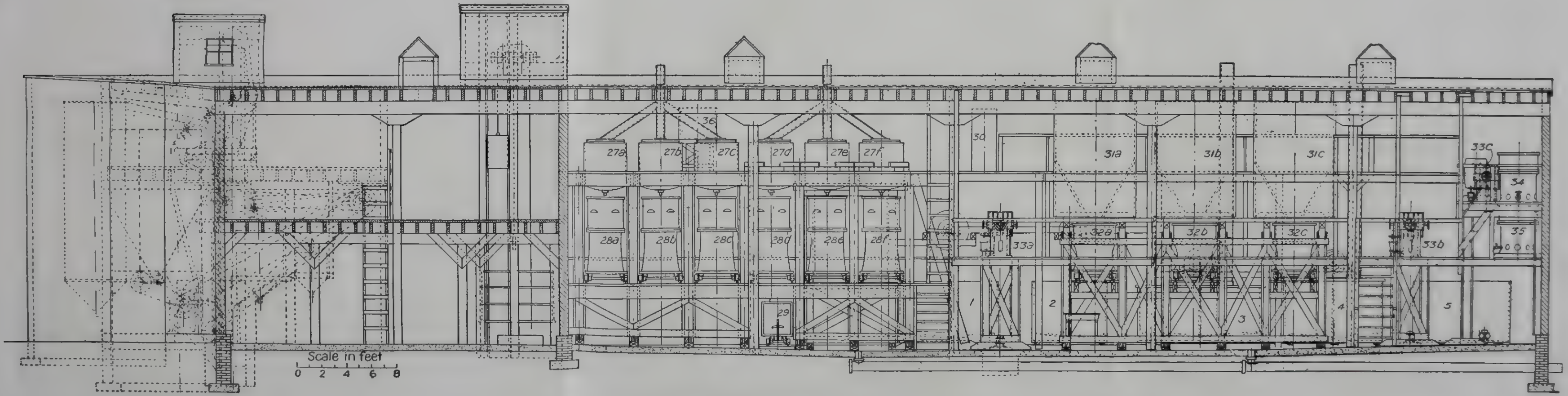
There was considerable difficulty in getting these tanks tight. Ordinarily, wooden tanks are built to hold water and any small leaks are closed by the swelling of the wood. When acid solutions are poured into wooden tanks, the wood tends to contract, rather than to swell, so that acid tanks must be set up differently. The staves must be properly machined and all joints made with special care, extra lugs must be used, and the use between the staves of a rubber cement is advisable. A tank must be absolutely tight when liquid is first put in. However, if these precautions are taken, a tank can be kept tight without serious trouble, an occasional tightening of the lugs or a little calking being all that is required. Oval holes were cut in the lower part of the tanks large enough to allow a workman to crawl in and thus get at the lugs holding the conical part of the tank (see Pl. X, *A*, p. 50). The lugs and, indeed, the whole exterior of the tanks should be kept covered with graphite paint. The other tanks were put up with a thin coating of white lead between the staves.

It has been found convenient to run the sodium carbonate into the tanks by bringing it on a small truck by means of the elevator (Pl. IV, A) to the third landing, and then letting it fall into the tank below through a wooden chute 8 inches square.


Dust Collector
Bin
Fan
Elevator
Elevator
Screen
37
36
30
34
35
27a
27b
27c
27d
27e
27f
33a
31a
31b
31c
33b
33c
Scale in feet
0 2 4 6 8

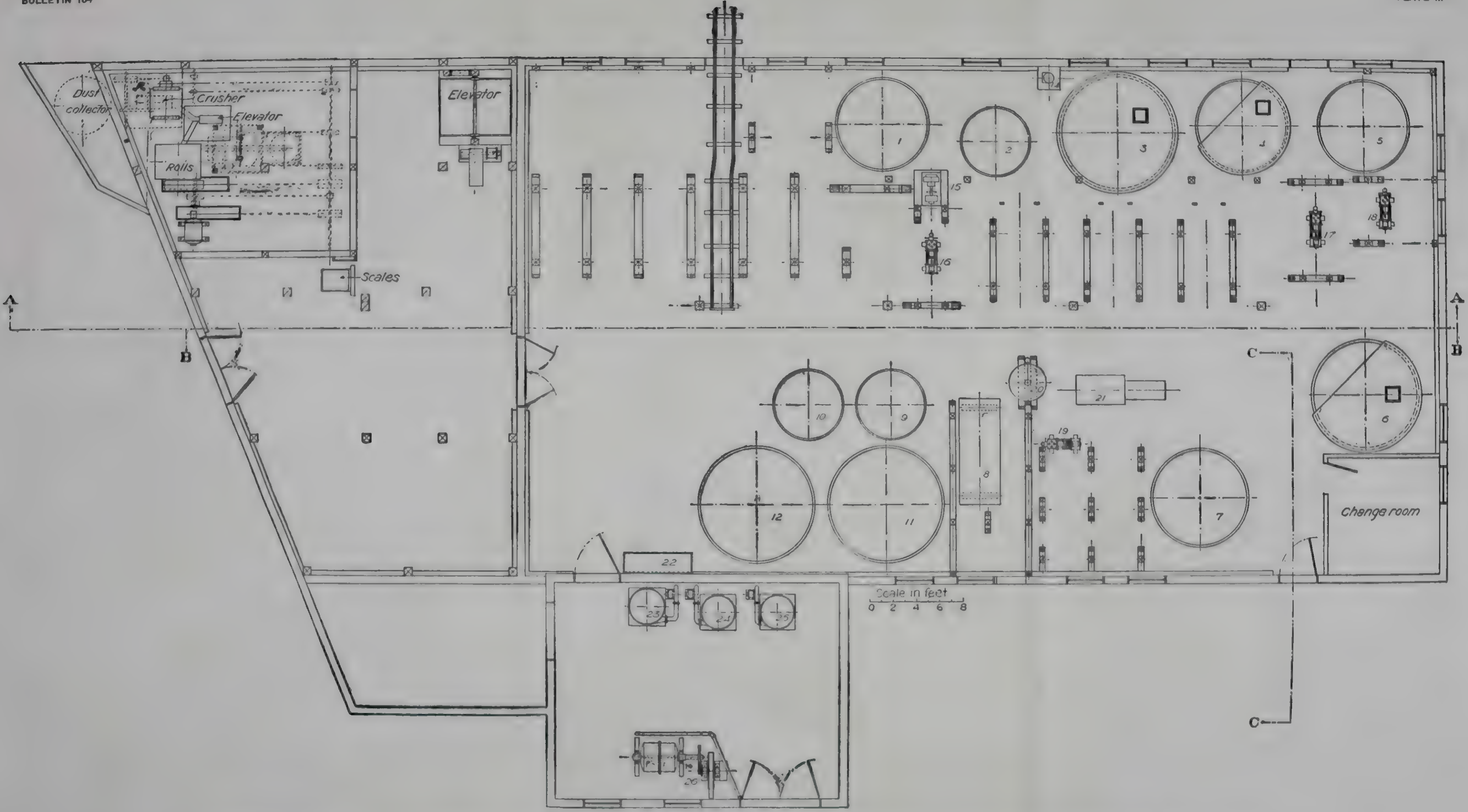
A. PLAN OF UPPER LANDINGS SHOWING SOUTH SIDE OF FIRST PLANT.

27a, 27b, etc., leaching pots and suction filters; *30*, sodium hydroxide tank; *31a, 31b, 31c*, settling tanks and filters; *33a, 33b, 33c*, filter presses; *34*, leaching pot; *35*, earthenware filter; *36*, dilute-acid tank; *37*, vacuum pumps.


36
30
27a
27b
27c
27d
27e
27f
31a
31b
31c
33c
34
28a
28b
28c
28d
28e
28f
33a
32a
32b
32c
33b
35
29
1
2
3
4
5
Scale in feet
0 2 4 6 8

B. SECTION OF FIRST PLANT THROUGH A–A, PLATE III.

1, radium precipitation tank; *2*, redissolving tank; *3*, sodium carbonate tank; *4*, uranium oxide tank; *5*, uranium recovery tank; *27a, 27b, etc.*, leaching pots; *28a, 28b, etc.*, suction filters: *29*, tram car: *30*, sodium hydroxide tank; *31a, 31b, 31c*, settling tanks; *32a, 32b, 32c*, suction filters; *33a, 33b, 33c*, filter presses; *34*, leaching pot; *35*, earthenware filter; *36*, dilute-acid tank.


Dust collector
Crusher
Elevator
Elevator
Rails
Scales
A
A
B
B
C
C
1
2
3
4
5
6
7
8
9
10
11
12
15
16
17
18
19
20
21
22
23
24
25
26
Change room
Scale in feet
0 2 4 6 8

FLOOR PLAN OF OLD OR "FIRST" PLANT.

1, radium precipitation tank; *2*, redissolving tank; *3*, sodium carbonate tank; *4*, uranium oxide tank, *5*, uranium recovery tank; *6*, sodium uranate tank; *7*, vanadium tank; *8*, distilled-water tank; *9*, *10*, storage tanks; *11*, *12*, sodium nitrate storage tanks; *13*, sulphuric acid elevating tank (not shown) is on platform outside of building, opposite distilled-water tank *8*; *14*, steam trap, *15*, centrifugal pump; *16*, *17*, *18*, *19*, pumps; *20*, steam baffle; *21*, compressor; *22*, steam dryer; *23*, barium sulphate reduction furnace; *24*, *25*, uranium furnaces; *26*, ball mill.

STEAM-HEATING DEVICES.

Each tank in which solutions are boiled contains a grid composed of 1½-inch Byers pipe with cast-iron fittings, the extent of heating surface in the different tanks depending, of course, on the object to be attained. In the larger tanks (10 to 12 feet in diameter) in which liquids are heated without being evaporated, 12 lengths 6 feet long have been found sufficient. In the nitrate storage tanks, where a certain amount of evaporation is desired, the heating surface is nearly twice that for the larger tanks. The steam flowing to these grids passes through a large baffle (*20*, Pls. V, VI, and VII) filled with vitrified brick, which eliminate impurities carried from the boiler. As the grids are also connected with suitable traps, a constant supply of distilled water is obtained and stored in a large iron tank (*8*, Pls. V, VI, and VII). From this tank distilled water is piped to the third landing to a point near the leaching pots, and by means of compressed air the water is elevated to this point whenever desired. As it is usually hot considerably less steam is needed in connection with leaching than if the water were cold. Exhaust steam is used for preliminary evaporation of the nitrate solutions.

FILTER PRESSES.

The filter presses used in the first plant are of the Shriver two-eyed "washing" type. The two larger presses (*33a*, *33b*, Pl. IV) contain 30 plates, each 24 by 24 inches. The smaller presses (*33c*, Pl. IV, and *33d*, Pl. V) contain 21 plates each, 18 by 18 inches. The iron precipitate press (*33a*, Pl. IV) is filled twice during the day's run, so that if one desired to empty this press only once a day, its capacity would have to be doubled. The small presses take care of the uranium and vanadium at one operation. Besides being connected with the tanks, the presses are piped for both water and compressed air. The pumps (*16* to *19*, Pl. III) connected with these presses are of the brass-lined, double-acting Worthington type.

ACID CONVEYORS.

The acid from the radium precipitating tank is elevated to the settling tanks by means of a centrifugal pump through 2-inch acid rubber hose. The parts of the pump that come in contact with the liquid are made of duriron, and have resisted the acid excellently, as has the rubber hose, which is lined with pure gum. The acid is transferred to any desired settling tank by running it through the hose into a wooden flume connecting the different tanks.

FLOATING SIPHON.

The floating siphon (Pl. X, *B*, p. 50) consists of a square wooden frame through the center of which a 1¼-inch acid hose extends about 18 inches, or any other desired length. The frame is built so that it settles in the tank until at a certain point it rests on the sloping sides of the cone. The length of hose going through the frame is long enough to siphon off the clear liquid above but not to disturb the radium-barium sulphate precipitate. The other end of the hose is connected with a 1½-inch piece of glass tubing 5 feet long, from which another piece of the same type of hose runs into the tank. An earthenware stopcock is inserted at a convenient point near the glass tube, and is held by a chock so that the cock can be turned but can not be forced out by the pressure of the liquid. In this way the flow of the liquid can easily be controlled, and at the same time the liquid can be examined as it runs through the glass tube. As long as it is not turbid it is free from radium-barium sulphate precipitate. If the workmen, in occasional inspection of the tube, note any turbidity they can shut off the siphon and thus eliminate radium losses. In running the acid liquid into the carbonate tank, any convenient form of spreader can be used to prevent much acid striking the carbonate solution at any one point and thus reducing too much the alkalinity of the liquid at that point.

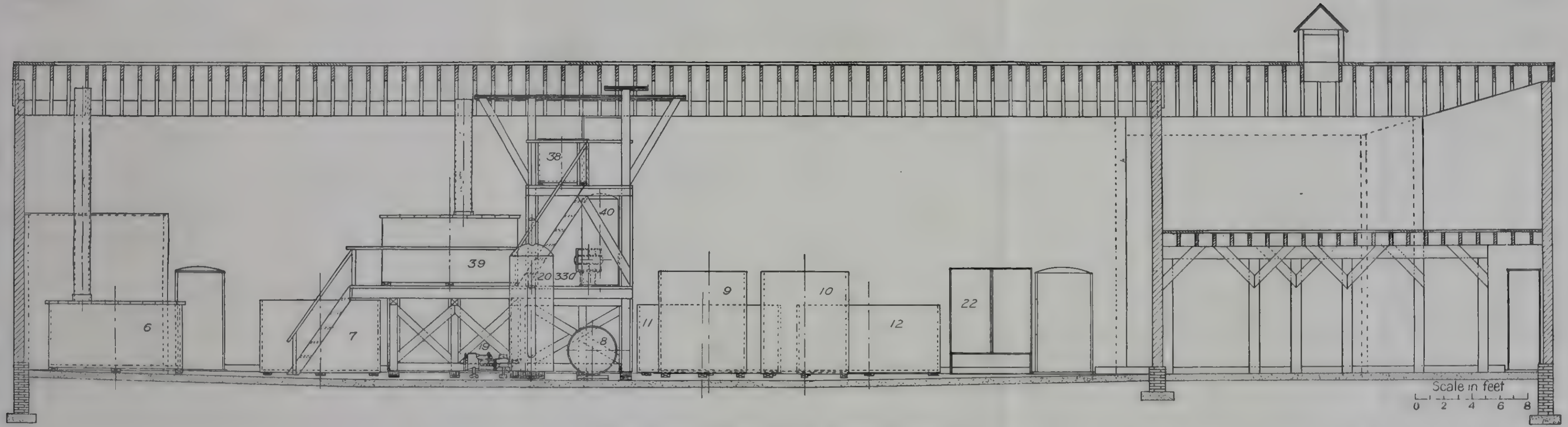
MISCELLANEOUS FEATURES.

After the clear liquid has been siphoned off, the radium-barium sulphate with the remaining liquor is introduced onto earthenware suction filters, which are placed below the settling tanks. As mentioned previously, these filters are also of the Edda type, the upper and lower parts each holding 52¾ gallons of liquid. They are placed on small trucks running on tracks, so that they can be pulled from underneath the settling tanks and the radium-barium sulphate easily removed (Pl. X, *A*).

A compressor delivering about 300 cubic feet per minute was originally situated on the north side of the plant (*21*, Pl. III). When the second plant was built, however, this compressor was removed and a larger one (*55*, Pl. II) was placed in the boiler house and now serves both plants.

The mechanical stirrers in the different tanks are belt driven, one motor driving the stirrers in tanks *1* and *2* (Pl. III, and Pl. IV, *B*), and another one driving those in tanks *3* and *4*. The liquids in tanks *5*, *6*, and *7* are agitated by compressed air, as the weight of the precipitates is not large and the time of agitation is not long. The stirrers in tanks *1* and *2* are of wood and have two blades revolving 8 inches and 18 inches above the bottom of the tank, and the stirrers

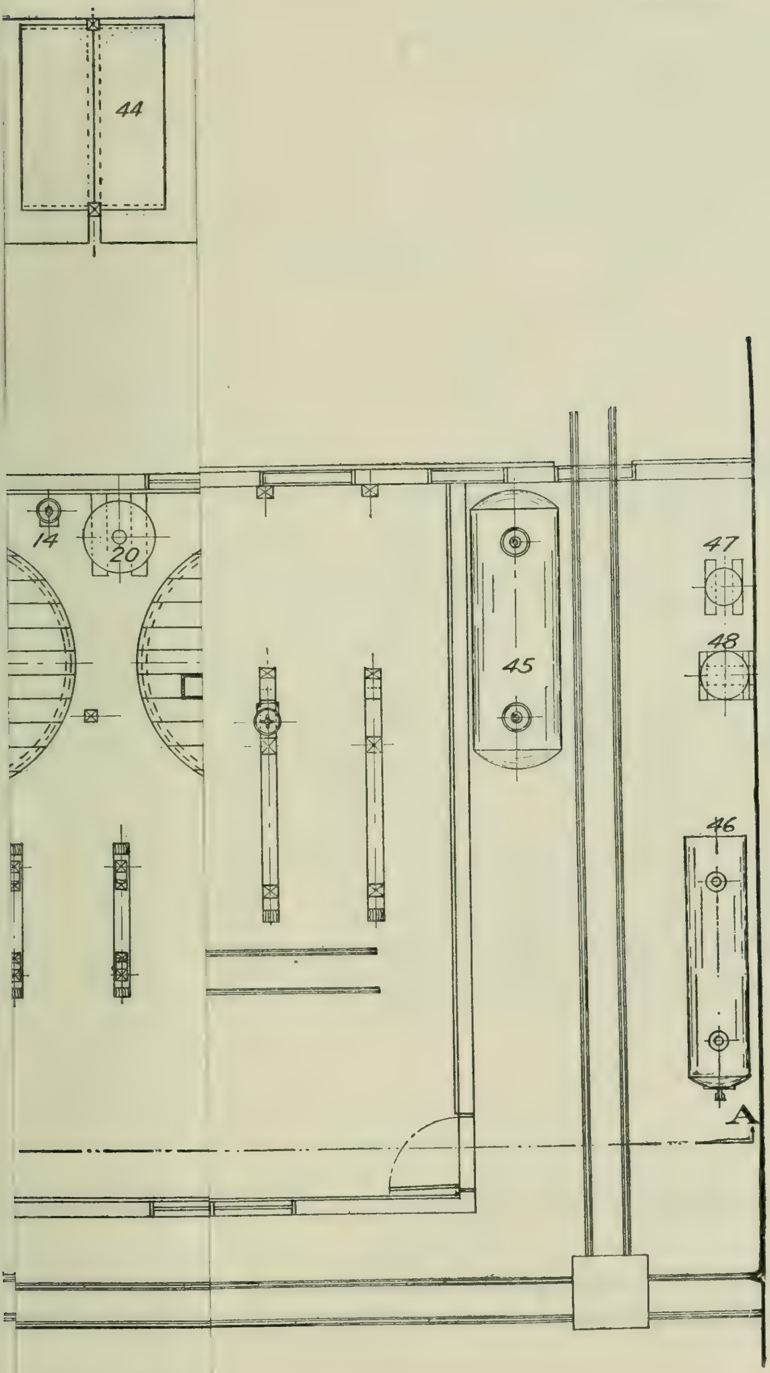
le; *22*, steam drier;


38
40
39
20
33d
6
7
19
8
11
9
10
12
22
Scale in feet
0
2
4
6
8

SECTION (REVERSED) OF FIRST PLANT THROUGH B B, PLATE III.

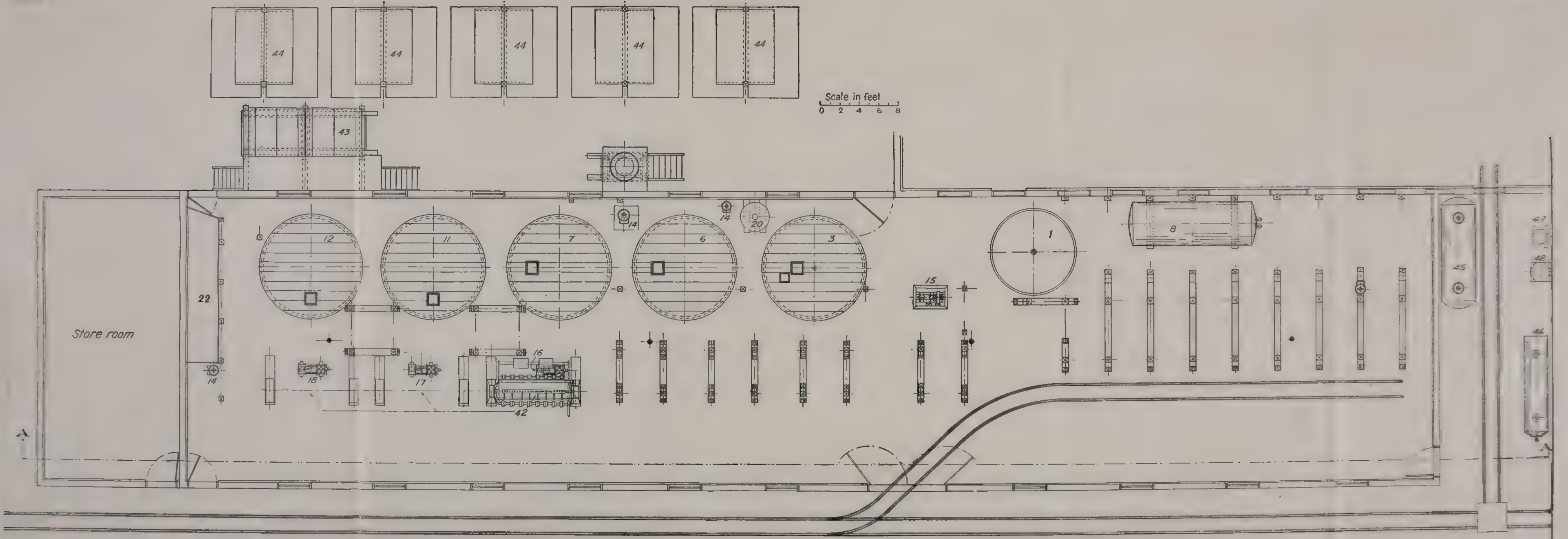
6, sodium uranate tank; *7*, vanadium tank; *8*, distilled-water tank; *9*, *10*, storage tanks, *11*, *12*, sodium nitrate storage tanks; *19*, pump; *20*, steam baffle; *22*, steam drier; *33d*, filter press; *38*, ferrous sulphate tank; *39*, vanadium tank; *40*, compressor tank.

PLATE VI


44
14
20
47
48
45
46
A

AN OF NEW OR “S

vanadium tank; *8*, dist
n nitrate evaporating t


44
44
44
44
44
Scale in feet
0 2 4 6 8
43
14
14
20
12
11
7
6
3
1
8
15
22
Store room
14
18
17
16
42
45
47
48
46
A
A

PLAN OF NEW OR "SECOND" PLANT.

1, radium precipitation tank; *3*, sodium carbonate tank, *6*, sodium uranate tank; *7*, vanadium tank; *8*, distilled-water tank; *11*, *12*, sodium nitrate storage tank; *14*, steam traps; *15*, centrifugal pump, *16*, *17*, *18*, pumps, *20*, steam baffle, *22*, steam drier, *42*, Sweetland filter presses, *43*, sodium nitrate evaporating tanks; *44*, sodium nitrate crystallizing tanks; *45*, sodium hydroxide tank, *46*, compressor tank, *47*, *48*, baffles

in tanks *3* and *4* are of iron, and each has one blade revolving just below the heating coil and a second blade about 6 inches above the heating coil.

DESCRIPTION OF SECOND PLANT.

The general arrangement of the second plant is similar to that of the first, but as the building had to be of a different shape, some changes were made, as well as some improvements.

Instead of using Shriver presses, three 25-inch, lever-operated, clam-shell Sweetland filter presses (Pl. VIII) were installed. Each one of these has 130 square feet of filtering surface. One takes care of the iron precipitate from the sodium carbonate tank, the other handles the uranium, and the third the vanadium. As the total capacity of the last two presses is larger than is required by the one plant, the uranium and vanadium from both plants are now filtered through these presses, the solutions carrying the precipitated uranium and vanadium in the old plant being pumped into the corresponding tanks in the new. These presses are piped for water, compressed air (on both sides of the cloths), vacuum, and steam. It has been found difficult to get the cakes from the presses sufficiently dry to be dumped easily without the use of compressed air.

The filtrates from the iron and uranium precipitates go directly from the pumps into elevated tanks (*51*, Pl. VII). From these the iron filtrates are run by gravity into the uranium-precipitating tank (*6*, Pls. III, VI, and VII), and the uranium filtrates into the vanadium tanks (*7*, Pls. III, VI, and VII, and *39*, Pl. V).

The stirrers in the new plant are driven by worm gears instead of belts. The stirrer in the radium-precipitating tank under load makes 44 revolutions per minute and that in the sodium carbonate tank makes 16 revolutions per minute. Each stirrer is driven by a -horsepower motor. The duriron centrifugal pump used for elevating the liquid from the radium-precipitating tank is the same size as was used in the first plant; it is run at 2,000 revolutions per minute and is belt-driven from a 5-horsepower motor.

The sodium hydroxide, which is used for partial neutralization of the acid in the radium precipitating tank, and also for precipitating the uranium, is made up in a steel tank (*49*, Pl. VII), placed on an exterior platform connecting the new plant and the boiler house. The sodium hydroxide in the iron drum is broken with a sledge hammer, and dumped into this tank, the solution being agitated with compressed air. It is advisable to use comparatively little hot water until all of the sodium hydroxide has been dissolved and the solution has cooled somewhat, when it can be diluted. The solution is then run by gravity through a pipe into a large steel storage tank (*45*, Pls. VI and VII), from which it can be transferred by means of compressed air to the measuring tanks (*30*, Pls. IV and VII), situated on the upper landing in each plant. By means of a float attached to a cord terminating in a weight, which rises and falls over a graduated scale, the amount of liquid taken from these tanks can be determined. From each of these measuring tanks pipes run to the radium precipitating tank and to the uranium tank in each plant.

The system for obtaining distilled water for the new plant is the same as that in the old, the distilled water reservoir (*8*, Pls. VI and VII) being correspondingly larger.

SULPHATE BUILDING AND EQUIPMENT.

The small building in which the radium barium sulphates receive preliminary treatment and fractionation (figs. 2 and 3) is situated just behind the first plant. The arrangement as shown in the plan (fig. 2) is not exactly the arrangement that actually existed at the time of writing (September, 1915) because the silica-lined, acid-proof kettles ordered in France had not arrived; the arrangement used was more or less tentative. The plan shows the arrangement as it will be when completed.

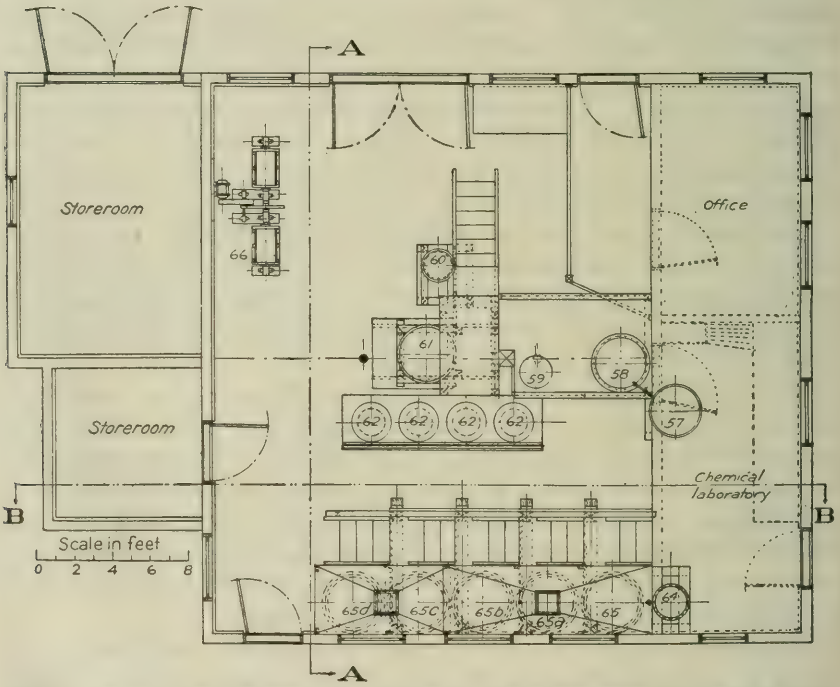
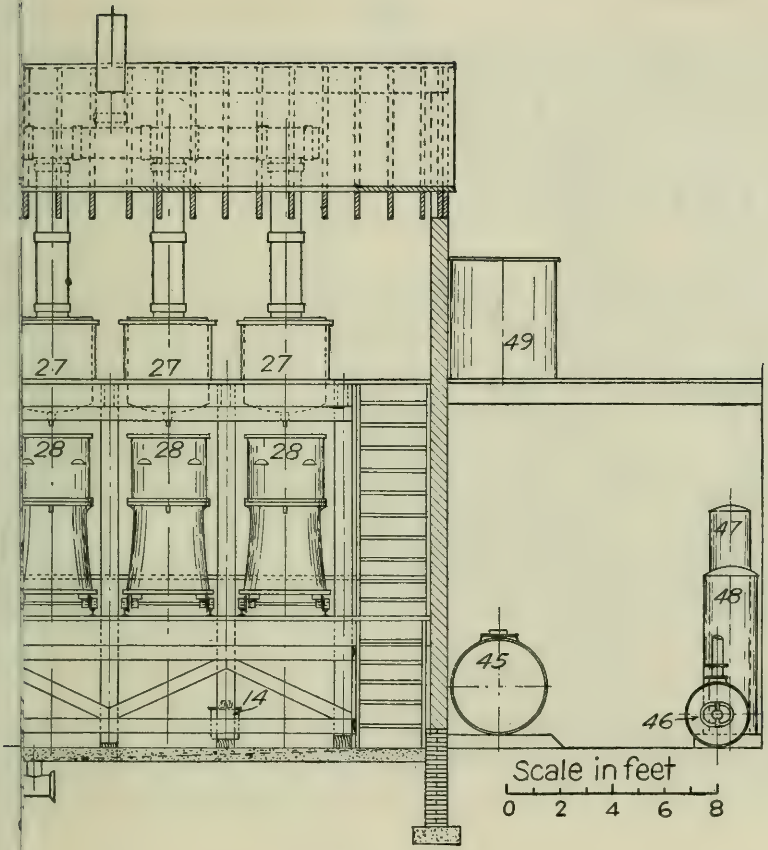


FIGURE 2.—Plan of sulphate building. *57*, condenser; *58*, distilled-water reservoir; *59*, baffle; *60*, experimental pressure apparatus; *61*, earthenware suction filter; *62*, silica-lined fractionating pot; *63*, dissolving pot; *64*, suction filter; *65*, *65a*, etc., steam-jacketed fractionating vessels; *66*, ball mills.

PLATE VII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27
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Scale in feet
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4
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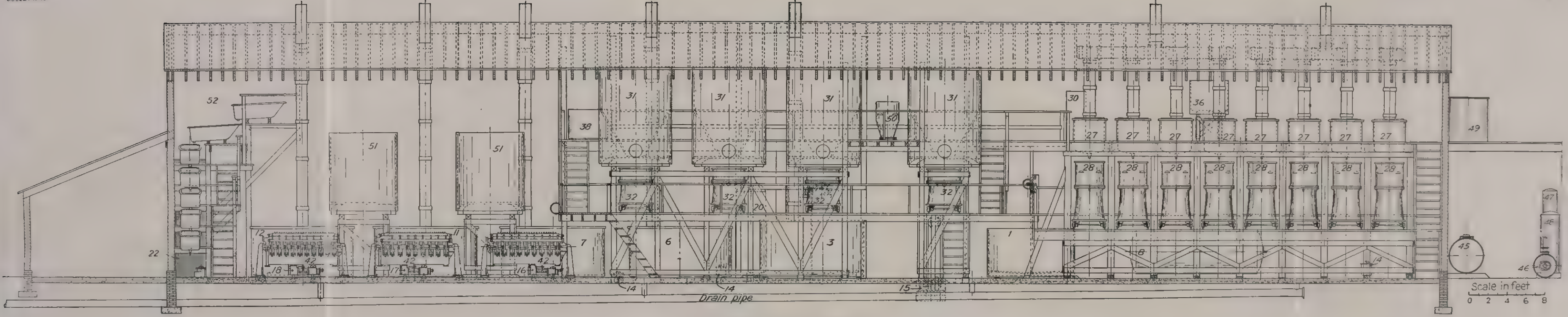
52
22
12
18
42
51
11
17
42
51
16
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7
38
31
32
6
14
31
32
20
14
Drain pipe
31
32
50
3
31
32
15
1
30
36
27
27
27
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27
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27
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47
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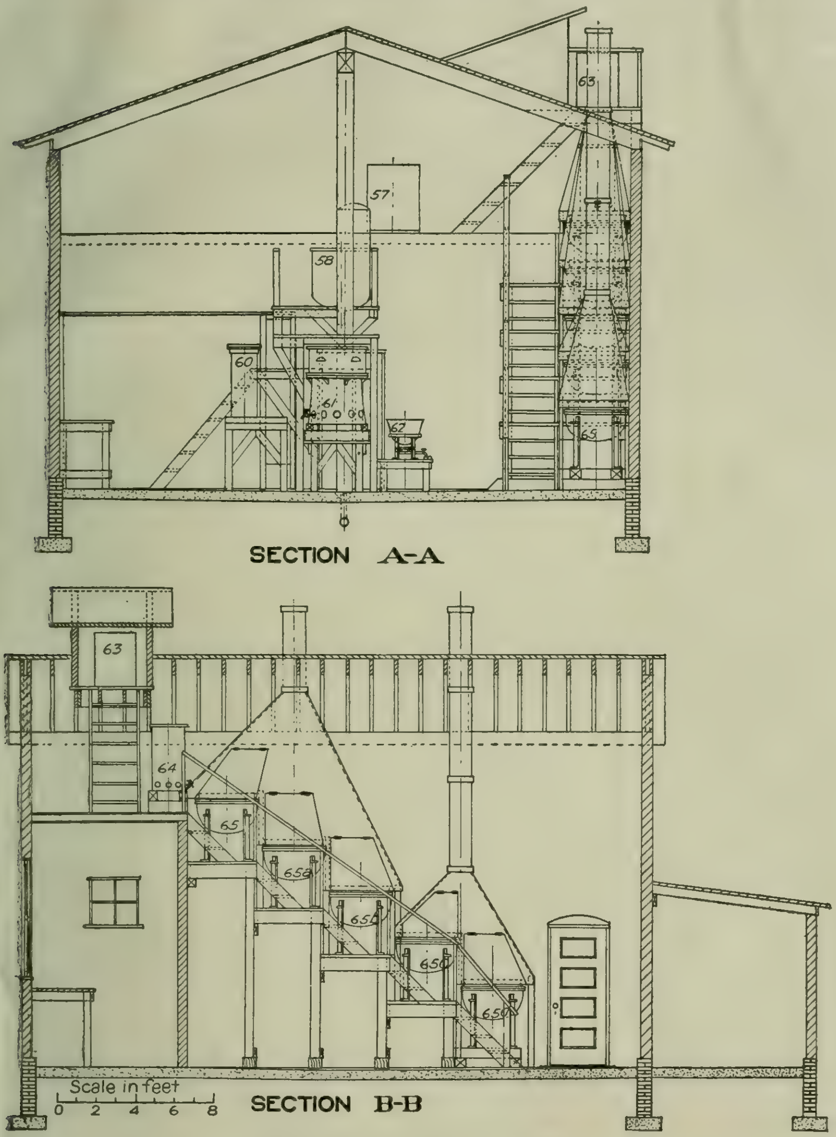
Scale in feet
0 2 4 6 8

SECTION OF SECOND PLANT THROUGH A A, PLATE VI.

1, radium precipitation tank, *3*, sodium carbonate tank; *6*, sodium uranate tank, *7*, vanadium tank, *8*, distilled-water tank, *11*, *12*, sodium nitrate storage tanks *14*, steam traps, *15*, centrifugal pump, *16*, *17*, *18*, pumps, *20*, steam baffle *22*, steam drier *27*, leaching pots, *28*, suction filters *30*, sodium hydroxide tank, *31*, settling tanks, *32*, suction filters, *36*, dilute acid tank, *38*, ferrous sulphate tank, *42*, Sweetland filter presses, *45*, sodium hydroxide tank, *46*, compressor tank, *47*, *48*, baffles, *49*, sodium hydroxide dissolving tank; *50*, earthenware pot for retreating sulphates, *51*, temporary storage tanks; *52*, gravity system of bath tubs

In order to crystallize radium-barium salts from acid liquors, it is, of course, necessary to a certain extent to evaporate the solutions, in order to get the concentration necessary for proper crystallization.


63
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SECTION A-A
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65a
65b
65c
65d
Scale in feet
0 2 4 6 8
SECTION B-B

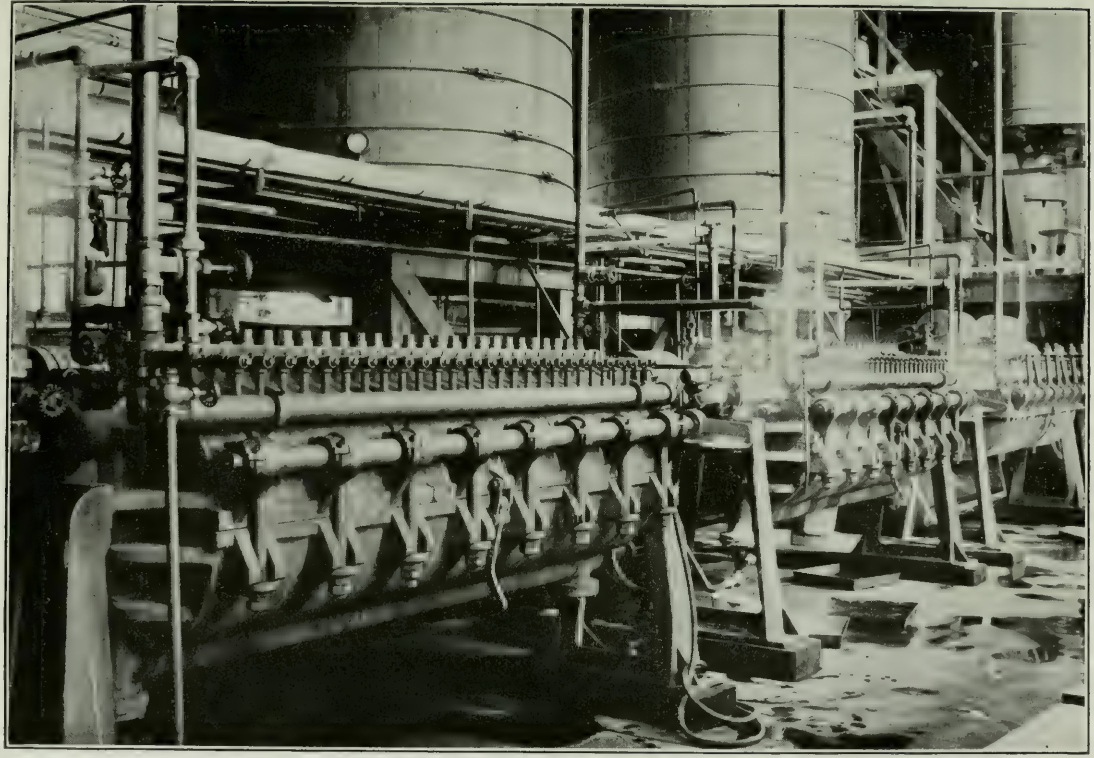
FIGURE 3.—Sections of sulphate building.

This might be done in earthenware vessels, provided a satisfactory and efficient method of heating could be obtained. Copper or silver steam coils might be used, but both of these metals are gradually attacked by concentrated hydrochloric acid, and in addition there would be a tendency for crystals to form around the coils. Breaking these crystals away would tend to damage the coils, and it would be inconvenient to handle the crystals under such conditions. Any exterior means of heating, such as steam, boiling water, or hot oil, would involve too great a risk of breakage of containers and loss of valuable solutions. Large silica or porcelain basins have been used, and when the table below them is covered with sheet copper bent up at the sides and ends and brazed, so as to make a shallow vessel, such dishes can be used with reasonable safety. Their capacity, however, is too small for handling the quantities of material required at the plant of the National Radium Institute; therefore, it became necessary either to have larger vessels that would stand the action of boiling concentrated hydrochloric acid, or else to crystallize in neutral solutions. As crystallization in acid is much more rapid and efficient, the former method is much to be preferred.

A silica-lined, acid-proof ware made by Danto-Rogeat & Co., of Lyons, France, is exceedingly satisfactory. No other ware obtained either in this or any other country gave satisfactory results. In fact, most of the so-called "acid-proof ware" failed absolutely to withstand the acid. The institute was able to procure a number of small-size vessels from Danto-Rogeat & Co., and also, through the courtesy of the Welsbach Co., of Gloucester, N. J., to obtain one 250-liter steam evaporator made by the same concern. Owing to the European war, Danto-Rogeat & Co. were unable to supply any large-size vessels, as they had none in stock and their factory was closed. In September, 1915, they were about to start operations again, and an order for a number of steam evaporators has been placed for the purpose of equipping the plant as indicated in figures 2 and 3.

Distilled water is obtained for this part of the work by passing live steam through baffle *59* (fig. 2), and thence through a 1-inch block-tin coil contained in condenser *57*, which consists of an ordinary wooden tank with the necessary inlet and outlet for a water flow. The block-tin pipe runs into earthenware distilled-water reservoir *58*, which has a capacity of 107 gallons, and the water is piped to any part of the building desired.

In the sulphate building are the office and a small chemical laboratory, which is used mainly for qualitative determinations, titration of acids, etc., or any chemical work in which a quick result is desired. The main chemical control work and radium measurements, as well as the final refining of the radium, has been done in the laboratories of the Bureau of Mines. There is also a small storeroom, built of reinforced concrete with a steel door, in which the radium-barium sulphates and other valuable material can be stored, so as to eliminate fire risk. The building also contains a small double ball mill,



VIEW IN NEW PLANT SHOWING FILTER PRESSES.

66, motor driven, for grinding the sulphates and mixing them with charcoal for later reduction in an oil furnace.

POWER HOUSE.

The 90-horsepower Kewanee locomotive-type boiler, used for the first plant alone, was purchased when the plant was on the experimental basis. When it was decided to build the second plant and continue work during the full period covered by the agreement with the Bureau of Mines, an additional 150-horsepower tubular Kewanee boiler was installed. The boiler house (Pl. II) is of brick, with concrete floor, a brick-and-iron partition separating the boilers from the compressor and pumps. The coal bin will readily hold about 2½ cars of coal.

The compressor (*55*, Pl. II) is 16 by 18 inches, capable of 140 revolutions per minute, and delivers about 650 cubic feet per minute at 40 pounds. The main vacuum pump *54*, a 10 by 20 inch Rotrex pump, belt driven, is connected with the suction filters used for leaching in both plants, and, with all pots connected, will give a vacuum of 20 to 22 inches of mercury. It is protected by means of a baffle, *47*, filled with brick, over which a strong solution of caustic soda slowly circulates. The small pump *54a* was the one originally used in the first plant, and was transferred to the powerhouse when the second plant was built. It is a No. 3 Nash vacuum pump; is chain driven, and will give a vacuum of 15 to 17 inches of mercury. It is connected with the suction filters under the settling tanks and also with the sulphate building, and is protected by a baffle (*48*, Pls. VI and VII).

Between the sulphate building and the extension of the new plant, is a small building with concrete floor and concrete walls for the storage of sodium nitrate. This building is connected by means of a belt elevator (Pl. XII, p. 60) with the bin in which the sodium nitrate is bedded and sampled, and from thence the nitrate is taken to the stills.

EQUIPMENT FOR SODIUM NITRATE RECOVERY.

The sodium nitrate is pumped from the storage tanks (*11* and *12*, Pls. III, VI, and VII) in each plant by means of a Worthington pump, 4½ by 2¾ by 4 inches, into the two evaporators (*43*, Pl. VI). These are made of ⅜-inch steel, one being welded and the other riveted, each being 6 feet by 5 feet by 24 inches, with a slope toward the center. Steam is used for evaporating, each tank containing a grid made of 1½-inch Byers pipe. Compressed air is used to hasten evaporation. The tanks are elevated so that the solutions can run by gravity into the crystallizing pans (*44*, Pl. VI, and Pl. XI, *A*), which are made of ⅛-inch steel. Each pan is 10 feet long by 5 feet wide, 8½ inches deep at one end and 12 inches at the other, sloping toward the deep end so that it will drain readily. The pans are protected by a wooden roof covered with elaterite.

FURNACE ROOM.

When the second plant was built, the original boiler house was converted into a furnace room. This is equipped with three Case oil furnaces (*23*, *24*, *25*, Pl. III), the blast being furnished by fans driven by 1-horsepower motors. The oil is supplied under pressure from a tank outside the building. The furnaces were specially built, two of them (*24* and *25*) holding cast-steel pots 18 inches high by 16½ inches wide and three-fourths of an inch thick (Pl. XI, *B*, p. 58). The other (*23*), a little larger in size, holds three No. 100 graphite crucibles, and is used in the reduction of the radium-barium sulphate. In the same room is a small ball mill (*26*, Pl. III), 2 feet 10 inches by 2 feet 6 inches, in which the sodium uranate is ground, either alone or with any other material that is desired in its treatment.

DETAILED DESCRIPTION OF OPERATIONS.

LEACHING.

HANDLING OF NITRIC ACID.

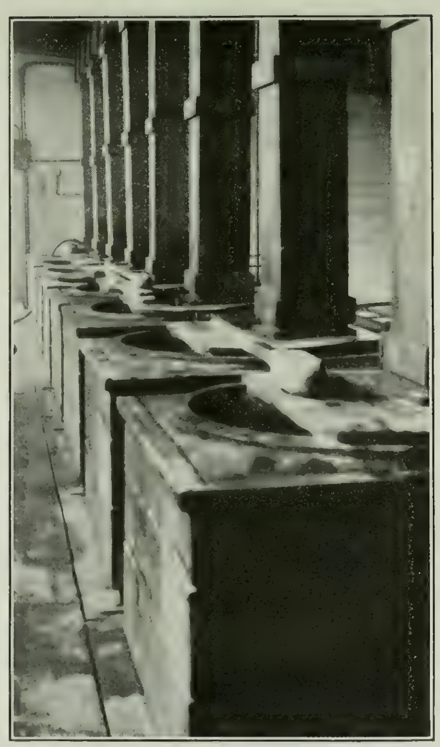
The nitric acid is handled in carboys, and was originally weighed on scales at the foot of the elevator close to the sampling room. Since the completion of the acid plant (Pls. XII and IX, *A*) it has been weighed as drawn from the storage pots. With the weighed ore it is carried by means of the elevator to the upper landing of the first plant, from which there is a connection to the upper landing of the new plant, so that the same elevator serves both plants.

The spout of each leaching pot (fig. 1) is filled with freshly washed sand in order to protect the rubber stopper, and the acid is then dumped from the carboys into the leaching pots (Pl. IX, *B*), each of which contains sufficient distilled water so that when the pot has been filled it contains 121 pounds of 100 per cent nitric acid diluted to 38 per cent strength. Each day the foreman in charge of this work receives a slip indicating the weight of acid to be weighed for each pot and the volume of distilled water to be added.

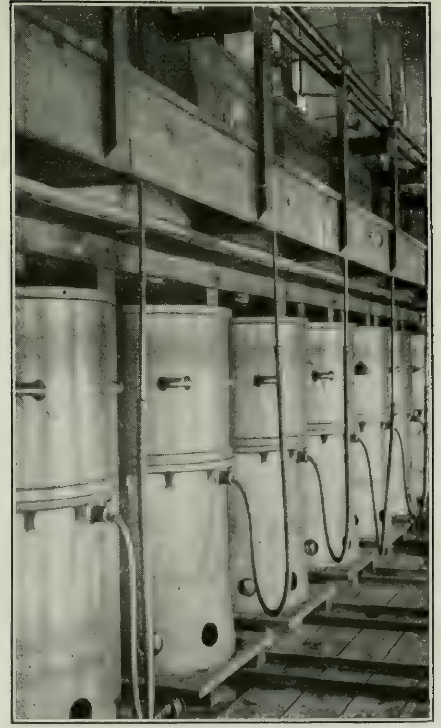
HEATING NITRIC ACID.

Live steam is run into the acid through a ½-inch glass tube connected by rubber tubing with a steam line. The steam in the line is passed through a baffle so as to eliminate impurities, and contains only traces of sulphates. As the distilled water is usually hot the

A. NITRIC ACID PLANT, FROM SOUTH.



B. BATTERY OF LEACHING POTS IN NEW PLANT.



C. SUCTION FILTERS IN NEW PLANT, SHOWING LEACHING POTS ABOVE.

time of heating is not long, but steam is run in until the temperature of the acid is at least 85° C.

The ore, ground to 20 mesh, is slowly added to each pot, the ore sacks resting on the wooden coverings (Pl. IX, *B*) on the pots, and the workmen using wooden paddles (Pl. IX, *B*) to stir the acid as the ore enters. Frequently calcium carbonate in the ore causes effervescence, and care has to be taken that the ore is not added so rapidly that frothing makes the acid overflow. Five workmen and a foreman can handle the 14 pots that are in the two plants and do all the necessary work connected with this part of the process. The heat of solution makes the temperature of the acid gradually rise during the addition of the ore, the temperature finally reaching 91° or 92° C. The addition of steam continues for 15 minutes after the last of the ore is in, the workmen stirring the different pots as rapidly as possible during this heating.

Nitric acid is not a very good solvent of vanadium, although it readily breaks up the vanadium minerals, even roscoelite. On the other hand, if too much vanadium is present, there is a tendency for vanadic acid to separate out in the acid as a reddish-brown precipitate. As this is rather gummy it retards filtration. If considerable vanadium separates in this manner, filtration may be so retarded that the acid cools down, causing a considerable loss of radium by reprecipitation. If there is little or no separation of vanadium in the acid, filtration takes place readily and quickly, and the extraction of the radium is thereby increased. Therefore, if the heating is continued with the object of decomposing the vanadium minerals other than carnotite, there is likely to be a loss of radium that will much more than compensate for the increased yield of vanadium. Consequently, it is much better not to continue the heating too long, but to make the extraction of the radium the main object. The uranium is practically all dissolved under the conditions mentioned.

USE OF HYDROCHLORIC ACID.

The addition of a small amount of hydrochloric acid to the nitric acid increases the solvent action on the radium. Therefore, if the nitric acid does not contain hydrochloric acid, enough hydrochloric acid is added to make the proportion of concentrated hydrochloric acid to 100 per cent nitric acid, about 2.5 per cent. In other words, to each pot, 9 pounds of 28 per cent hydrochloric acid, the strength of the acid available in Denver, is added. This hydrochloric acid, of course, appears as sodium chloride mixed with the sodium nitrate, and the nitric acid made from the sodium nitrate contains some hydrochloric acid.

When heating has continued long enough, a wooden plug on the end of a long handle is inserted into the pot and pushed through the ore until it almost completely stops the inside opening of the spout. By means of a lever (fig. 1) the rubber stopper is then removed from the lower part of the spout, and by raising the plug a little the acid is allowed to run onto the upper part of the suction filter (Pl. IX, *C*) below. In this manner, the flow of acid can be readily controlled, and at the same time a considerable part of the ore is retained in the leaching pot and receives the benefits of the acid wash. Thus, this method of handling the material has partly the effect of decantation.

USE OF ACID WASH.

An acid wash that has been prepared and heated in a small wooden tank, of which there is one in both plants (see *36*, Pls. IV and VII), is run into each pot, and the heating, by means of live steam, continues. The acid flows by gravity through an acid-proof rubber hose, and each pot receives an acid wash of about 170 pounds of 10 per cent nitric acid. When the acid leach on the suction filters has gone through, the acid wash, with the remainder of the ore, is dumped onto the filters in the manner described above.

WASHINGS WITH DISTILLED WATER.

When this material has completely filtered, the ore receives two washes of hot distilled water of 200 pounds each. Before the distilled water is added, however, the vacuum is broken on the filters and the liquid below, which consists of the acid and acid wash, runs from the bib cocks with which each filter is provided and flows through an earthenware pipe, which connects the different filters, to the radium precipitation tank (*1*, Pls. III, IV, VI, and VII). This tank contains 5 or 6 inches of water so that the hot acid is diluted enough not to damage the tank seriously. When the distilled water washes have filtered they are added in the same way to the acid liquor. Usually, the leaching process and filtration are complete between 2 and 3 o'clock in the afternoon. While the filtering is actually under way the workmen are weighing out the acid and ore for the next day's run, and transporting it from the first floor to the third, so that leaching on the next day can begin promptly. As soon as filtration is complete the residue, consisting mainly of silica, is shoveled from the upper parts of the filters into a small trolley, which runs along the platform on which the filters are placed, and hauled to the dump.

ADDITION OF SODIUM HYDROXIDE.

The acid solution in the radium precipitation tank (*1*, Pls. III, IV, VI, and VII), together with the wash water, is partly neutralized with sodium hydroxide, which is contained in small iron reservoir tanks

(*30*, Pls. IV and VII). The tanks are filled as needed through pipes from the main sodium hydroxide reservoir (*45*, Pls. VI and VII), the liquid being propelled by means of compressed air. Sodium hydroxide is added at first rapidly and then slowly, the solution being stirred all the time. After a certain amount of the sodium hydroxide has been added a greenish precipitate appears in the tank. As more alkali is added this precipitate gets heavy and finally tends to turn slightly brown. At this stage the addition of the alkali should stop. As a rule, about 70 pounds of sodium hydroxide is required per ton of ore treated, but no set rule as to quantity can be given, as the iron and vanadium content of the ore varies. The more iron and vanadium the ore contains, the less sodium hydroxide can be added without carrying the precipitation too far.

RADIUM PRECIPITATION.

About 2 pounds of barium chloride, in solution, per ton of ore treated is then poured into the tank. As a rule the barium chloride is that recovered in fractionation and contains small quantities of radium. After the solution has been stirred for five minutes in order that the barium chloride may be well mixed in, sulphuric acid is added, about 15 pounds of 100 per cent acid per ton of ore treated. The sulphuric acid not only precipitates barium sulphate, which carries down the radium, but also dissolves the small precipitate of iron and vanadium in the solution. Consequently the final precipitate obtained is a fairly clean one of radium-barium sulphate, containing only small traces of iron, vanadium, etc.

Should the addition of the sodium hydroxide be carried too far, the precipitate obtained is what is called a "retreat"; that is to say, it carries more iron and vanadium than is advisable. Under such conditions the wet sulphate is placed in an earthenware pot (*50*, Pl. VII) and concentrated sulphuric acid is added, the whole being thoroughly stirred. Water is then run in and the iron and vanadium readily dissolve in the hot liquor obtained, leaving the radium-barium sulphate as a clean white residue. The liquid and residue are run through a rubber hose to one of the filters (*32*, Pl. VII). Each filter is used only one day out of four for filtering the regular precipitate from the settling tanks (Pl. X and *31*, Pl. VII). The amount of sulphuric acid required for leaching a retreat varies according to the amount of iron and vanadium in the precipitate, but usually 25 to 35 pounds of 66° B. acid suffice. The acid filtrate obtained is used as part of the sulphuric acid required for precipitating the next batch of radium-barium sulphate in the precipitation tank (*1*, Pl. VII).

After the precipitation of the radium-barium sulphate, stirring is continued for one hour, when the whole solution is pumped into one of the settling tanks (*31*, Pl. VII) through the centrifugal pump (*15*, Pls. III, VI, and VII). In the first plant the settling process occupied three days, as there were only three settling tanks; in the second plant the liquids are allowed to settle four days, there being four tanks. On the second day after the liquid has been run into the tank a solution containing 1 pound of barium chloride is poured in and thoroughly stirred into the upper part of the acid liquor by means of a paddle. The object is to carry down any small traces of radium that may have remained suspended or dissolved in the supernatant liquid.

PRECIPITATION PROCESSES.

IRON PRECIPITATION.

USE OF SODIUM CARBONATE.

When the settling is complete the clear liquid above the precipitate is siphoned off through a 1¼-inch acid rubber hose attached to a floating siphon. The acid liquor is run into tank *3* (Pls. III, VI, and VII), which contains a hot solution of sodium carbonate more than sufficient to neutralize the acid. The weight of sodium carbonate used depends to some extent on the character of the ore treated. The smaller the amount of uranium and vanadium in the ore, the smaller the excess of carbonate required. For ore running from 2.5 to 3 per cent U_3O_8,[a] 250 pounds of excess sodium carbonate is required per ton of ore treated. This figure does not take into consideration the addition of the sodium hydroxide in the radium precipitation tank, but is calculated on the original acidity of the acid used. Consequently if acid of the strength and in the quantity described under the section on leaching is used the actual weight of sodium carbonate used is about 650 pounds of soda ash per ton of ore. In reality the excess of sodium carbonate is larger than that indicated, owing to the fact that a part of the acid is neutralized by the sodium hydroxide added in tank *1*. A 2 per cent U_3O_8 ore would not need more than 200 pounds excess sodium carbonate per ton of ore unless it contained more than the usual amount of vanadium.

The acid liquor is siphoned into the hot sodium carbonate, the whole process taking about three hours. As long as the alkali is in excess, there is little chance of the solution boiling over; should the neutralization point be nearly reached, there is serious danger of such boiling. The liquid is heated during the addition of the acid, and maintaining the temperature near the boiling point during the entire period is important; otherwise the precipitate, which should be red, becomes brown or even bluish-brown, and carries considerable vana-

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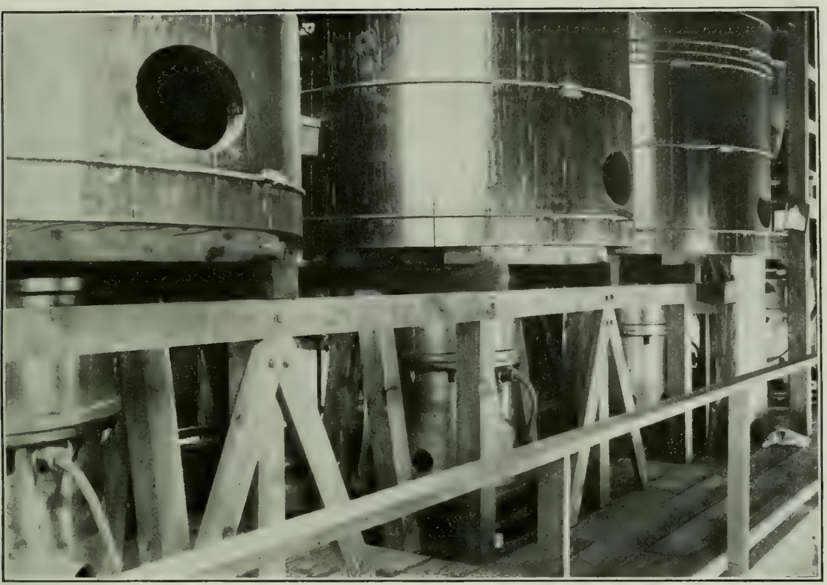
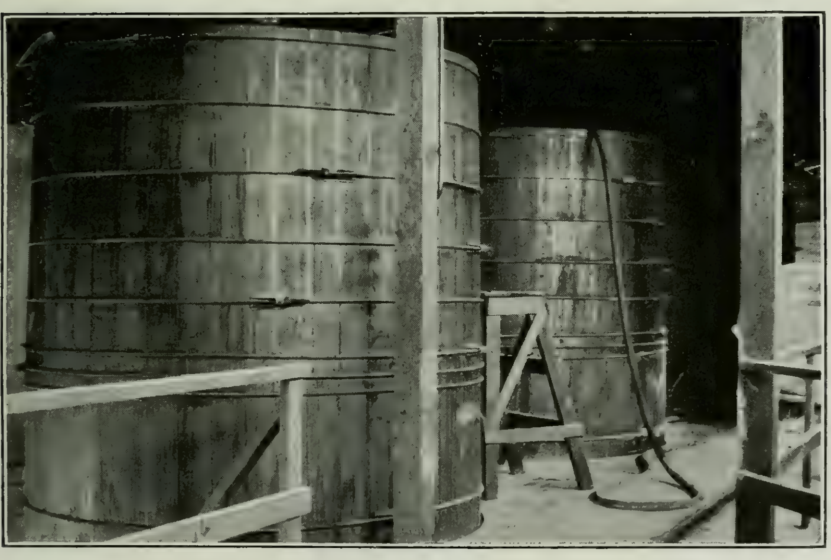
[a] The term "U_3O_8" is used here, and in a similar connection in other pages, as a basis of calculation, because it is the basis now universally used in commerce when ores are purchased or sold. Strictly speaking, the symbol should be "UO_3."



A. LOWER PART OF SETTLING TANKS, WITH EARTHENWARE FILTERS BELOW.



B. UPPER PART OF SETTING TANKS, SHOWING FLOATING SIPHON.

dium and too much uranium. Not only is the amount of sodium carbonate in excess important but also the time of boiling after the acid has been completely added. In actual practice, the boiling is continued for three hours after the last of the acid has been run into the tank. There are, therefore, two important factors that control the amount of uranium and vanadium left in the precipitate, namely, the excess of sodium carbonate and the period during which boiling is continued, the latter being just as important as the former.

FILTERING THROUGH PRESSES.

The solution is then filtered through filter presses—in the first plant through press *33a* (Pl. IV); in the second plant through press *16* (Pls. VI and VII), the filtrates running into tanks *6* (Pls. III, VI, and VII), in which the uranium is afterwards precipitated. The precipitates are washed in the filter press for about 20 minutes, the washing being added to the original solution. It is, of course, advisable to wash the precipitates until they are as free as possible from adhering liquor so as to decrease the loss on uranium and vanadium, but the amount of washing is controlled by the capacity of the tanks into which the filtrate is run.

The uranium and vanadium content of the iron precipitate obtained has varied considerably, the average uranium content running about 0.7 per cent U_3O_8, and the average vanadium content about 2 per cent V_2O_5. Some of the precipitates have gone as low as 0.5 per cent U_3O_8 and 1 per cent V_2O_5, whilst once or twice, when there was a temporary lack of steam and the boiling was not continued sufficiently long, the uranium content of the iron precipitate was more than 2 per cent U_3O_8.

RECOVERY OF BARIUM SULPHATE PRECIPITATE.

After the acid liquor has been added to the sodium carbonate tank, as described above, and before the filter-pressing of the iron precipitate, the radium-barium sulphate precipitate in the conical settling tanks is run through earthenware stopcocks at the bottom of each settling tank onto the suction filters. The solution is filtered under suction, and, by means of a rubber hose attached to the spout of the filter, the filtrate is added to the sodium carbonate tank. The sulphate is washed with distilled water, and with a weak solution of sodium hydroxide, in order to neutralize any adhering traces of acid. It is then carefully scraped from the filter paper placed over the asbestos filter cloth and is put into an iron pan 19 by 20 by 3 inches. The sulphate is dried in a hot-air oven heated by steam coils, after which it is transferred to the sulphate building for further treatment. If the solution at any time runs through cloudy, owing to the presence of barium sulphate in the filtrate, it is run back into tank *1* (Pls. III, IV, VI, and VII) by means of a long rubber hose, and the sulphate that has gone through the filter is thus recovered with the next radium-barium sulphate precipitate. It is found preferable to do this rather than to try to refilter the solution at once. Such mechanical losses in plant operation should be carefully watched, as they are more likely to occur than chemical losses.

RE-SOLUTION OF IRON PRECIPITATE.

When the first plant was started it was thought that not only would the recovery of the uranium and vanadium content of the iron precipitate be justified, but also that the radium not recovered in the first radium-barium sulphate precipitate might be sufficiently large to justify its recovery also. Therefore, the original plan of procedure involved the re-solution of the iron precipitate in hydrochloric acid and the precipitation of a second radium-barium sulphate precipitate, followed by a second precipitation with sodium carbonate.

Accordingly, into tank *2* in the first plant was poured a sufficient amount of commercial hydrochloric acid to just dissolve the iron precipitate. This was diluted with an equal volume of water. The amount of acid required varied with the ore treated. Some ores carry more iron than others, and, therefore, the exact quantity of hydrochloric acid required in all cases can not be stated. In addition, if the iron precipitate carried a little more vanadium than usual, this affected the quantity of acid required. Generally speaking, however, 950 pounds of 28 per cent hydrochloric acid was required for each ton of ore treated. The acid was used cold, the iron precipitate being added slowly, one shovelful at a time, the liquor being thoroughly agitated by a paddle during the addition. If the iron precipitate is added too rapidly, the solution heats, and toward the end of the reaction there is a tendency for the vanadium to separate. Under these conditions it is difficult to get the whole mass in solution, so that when the radium-barium sulphate is precipitated, an unsatisfactory, dirty sulphate is obtained.

When all the material is in solution the tank is almost filled with water and 3 pounds of barium chloride added. This is followed by the addition of 30 to 40 pounds of 66° B. sulphuric acid. The dilution and the amount of sulphuric acid added is affected, to some extent, by the amount of calcium in the ore, as calcium sulphate is likely to be precipitated if the solution is not sufficiently dilute.

The radium-barium sulphate thus obtained was elevated to one of the settling tanks and allowed to settle until the next day. The clear liquid obtained was siphoned off by means of a floating siphon, in the ordinary way, and run into an excess of hot sodium carbonate, the iron-calcium precipitate obtained being filter-pressed, and the uranium and vanadium in the filtrate recovered.

It was found that the cost of recovering this uranium and vanadium was greater than the value of the products obtained, and after a few trials, the second precipitation of uranium and vanadium was abandoned, and the tanks that were designed for use in this part of the process, namely, tanks *2*, *4*, *5*, and *7* (Pls. III, IV, *B*, and V) were afterwards used for other purposes. However, the second precipitation of the radium was continued for a longer period of time, "second" sulphates being obtained on the first eight cars of ore treated. Later, it was found that the recovery on one car (P–7) was not satisfactory, and that some of the radium was going through in the filtrate from the first radium-barium sulphate precipitate. The re-solution of the iron precipitate and the formation of second sulphates was again started at this time and continued with the ore from three cars (P–7, P–8, and P–9). As the cause of the losses was then ascertained to be of a mechanical nature, and eliminated, the formation of the second sulphates was again discontinued, as the amount of radium obtained in the sulphates did not justify the expense.

PRECIPITATION OF URANIUM.

The filtrate from the iron precipitate carries the uranium in solution as a double sodium uranyl carbonate and the vanadium as sodium vanadate. The solution is partly neutralized, acid being added until a yellow precipitate begins to form. This precipitate is supposed to be uranyl carbonate, but in reality it contains more sodium uranate than uranyl carbonate, as on ignition it gives a very small amount of oxide. If too much acid is added at this stage the amount of vanadium that appears with the sodium uranate is considerably increased. When the precipitate begins to foam the addition of acid is stopped and sodium hydroxide is added to the hot liquor until the uranium is completely precipitated as sodium uranate. The completeness of the precipitation is easily tested by filtering off some of the precipitate on a small funnel and adding more sodium hydroxide to the filtrate in the test tube or beaker.

During the operation of the first plant, before the second had been built and before a nitric-acid plant had been erected, sulphuric acid was used to partly neutralize the sodium carbonate. The sulphuric acid was run into the iron tank (*13*, fig. 4) and elevated by compressed air into the lead-lined tank (*41*, fig. 4), where it was diluted and run through lead pipes to the uranium-precipitating tank (*6*, Pl. III) and the vanadium tanks (*7*, Pl. III, and *39*, fig. 4 and Pl. V). Therefore the filtrate from the vanadium precipitate afterwards obtained contained not only sodium nitrate but also large quantities of sodium sulphate, and it was necessary to separate the sodium sulphate by means of fractional crystallization, as described subsequently. After the nitric-acid plant had been erected it was found much more satisfactory and, in the end, cheaper to neutralize at this point with nitric acid instead of with sulphuric acid, so that the grade of sodium nitrate obtained could be greatly increased and fractional crystallization could be eliminated.

After the addition of the sodium hydroxide and the precipitation of the uranium the solution is boiled for one hour in order to promote complete precipitation and is then filtered through press *17* (Pl. VI). This press takes care of the uranium in both plants, although originally the uranium precipitate in tank *6* (Pl. III) in the first plant was filtered through press *33c* (Pl. IV, *A*). The sodium uranate cake is washed for about 15 minutes and then dried in pans in hot-air ovens (*22*, Pls. V and VII). This method of drying has been found to be the best under the circumstances, not only for the radium-barium sulphate precipitates, but also for the uranium and the vanadium.

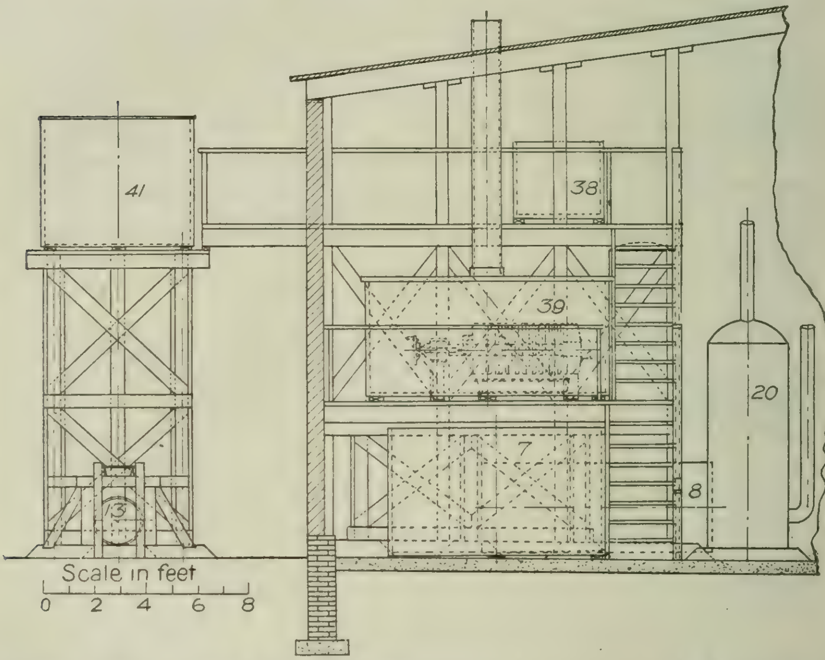


FIGURE 4.—Section of first, or "old," plant. *7*, vanadium tank; *8*, distilled-water tank; *13*, sulphuric acid elevating tank; *20*, steam baffle; *38*, ferrous sulphate tank; *39*, vanadium press; *41*, sulphuric acid tank.

Trial was made of another method, embracing the use of large iron pots heated by direct heat from a small fire placed beneath, but the results were not satisfactory; both the uranium and the vanadium precipitate caked readily and dried slowly, notwithstanding considerable hand stirring. The method, therefore, was abandoned.

As the sodium uranate requires re-treatment, owing to the fact that it carries vanadium, it is not necessary to wash the cake as completely as might otherwise be required. Most of the sodium uranate carries 7 to 9 per cent V_2O_5. It has been found practically impossible to obtain a precipitate that does not carry considerable quantities of vanadium, most of which appears probably as uranium vanadate.

PRECIPITATION OF VANADIUM.

The filtrate from the sodium uranate precipitate contains the vanadium as sodium vanadate. The solution is brought to the boiling point and just neutralized with nitric acid, the boiling being continued long enough to eliminate the carbon dioxide. A workman, after a little practice, is able to neutralize the solution and do the rest of the work satisfactorily. A solution of ferrous sulphate, made by dissolving ordinary commercial ferrous sulphate in cold water, is then run from small storage tanks (*38*, fig. 4 and Pls. V and VII) into the hot solution, agitation being accomplished by means of compressed air. The amount of ferrous sulphate added depends to some extent upon conditions, such as acidity, irrespective of the amount of vanadium present. As a rule, about 75 pounds of ferrous sulphate is required per ton of ore treated. The heating of the solution is stopped before the addition of the ferrous sulphate, for if heating is continued longer a complete precipitation of the vanadium is not obtained.

It is advisable to have the solution just neutral after the addition of the sulphate, and if it is neutral before this addition it will of course be slightly acid afterwards. It is difficult so to gauge the amount of acid added to the vanadium solution that the latter will be exactly neutral after the addition of the ferrous sulphate. In practice it is found convenient to make the solution exactly neutral before the addition of the ferrous sulphate and then to add a few pounds of sodium hydroxide to neutralize the solution once more after the addition of the ferrous sulphate. In this way practically all of the vanadium is precipitated as iron vanadate, only a mere trace going through in the filtrate. The precipitate is probably a mixture of the different vanadates of iron and has a greenish-gray color; it usually contains 32 to 33 er cent of V_2O_5.

It is not difficult to control the grade of the precipitate obtained. If the solution is slightly alkaline before the addition of the ferrous sulphate, a product carrying as low as 25 per cent V_2O_5 may be obtained. This is brown, with practically no green tinge. If the solution is faintly acid after the addition of the ferrous sulphate, a product may be obtained that is somewhat yellow and under favorable conditions may carry as much as 42 per cent V_2O_5. In other words, in a slightly acid solution, with continued boiling, a high-grade product is precipitated, but all of the vanadium is not recovered, some of it going into the filtrate. This contaminates the sodium nitrate and undoubtedly causes losses on evaporating the nitrate solution owing to decomposition.

If carnotite is treated in a beaker with nitric acid, filtered, the filtrate poured into an excess of hot sodium carbonate solution, the uranium precipitated by sodium hydroxide, and the vanadium precipitated by ferrous sulphate the product universally obtained is a dark-brown precipitate carrying less than 25 per cent V_2O_5. On a large scale oxidation is much more complete, and a much higher grade product can be obtained than in the laboratory. Seemingly this result is due not only to the long time during which the liquids are boiled, but also to the fact that air is being continually passed through them.

Before the erection of the nitric-acid plant the neutralization of the vanadium solution was accomplished by means of sulphuric acid instead of nitric acid. The change was made for reasons already indicated under the discussion of uranium precipitation.

NITRATE RECOVERY.

Before the second plant had been built, the evaporator and the crystallizing pans for the recovery of the sodium nitrate were placed in the angle formed by the first plant and the boiler house, which is now used as a furnace room. After the second plant had been added, the crystallizing pans were removed from their original position to that shown in Plate VI (*44*). An extra evaporator was also installed to take care of the increased capacity. The present equipment handles all of the nitrate solution from both plants.

As already stated, while the first plant was being operated by itself, the excess sodium carbonate in the uranium and vanadium tanks was neutralized by means of sulphuric acid, consequently the filtrate from the vanadium precipitate consisted of a neutral solution of sodium nitrate and sodium sulphate. It was necessary, therefore, in order to recover a sufficiently high grade of nitrate, to separate a considerable amount of the sulphate from the nitrate by fractional crystallization.

The filtrate from the vanadium precipitate was stored in tanks *11* and *12* (Pls. III and V) before the liquor was run into the evaporating pan. One of these tanks was fitted with a grid made of Byers pipe. Waste steam was run through the grid so that partial evaporation took place in the tank itself before the liquor was run into the evaporating pan, in which it was finally concentrated to a specific gravity of 1.23 to 1.27. As concentration was effected in the pan, more liquor was pumped from the storage tank. When a sufficient amount of the concentrated liquor had accumulated, it was run into a crystallizing pan (Pl. XI, *A*). The product obtained from this first crystallization, consisting mostly of sodium sulphate, varied somewhat in composition, the variation depending largely on the temperature of the air during crystallization. Usually, however, the wet salt carried between 3 and 10 per cent of sodium nitrate, the water content varying from 42 to 50 per cent, and was classed as "high-grade sulphate." As it could not be sold or even given away in Denver, most of it was dumped.

The mother liquor from the crystals was pumped back into the evaporator and concentrated to a gravity of 1.35 to 1.38, and allowed to crystallize. The product obtained from this crystallization was classed as "low-grade nitrate," and as with the first crystallization, the composition varied somewhat, according to the temperature of the air during the crystallization. Most of the wet product carried 30 to 35 per cent sodium nitrate and 20 to 30 per cent water. The liquor from the low-grade nitrate was further concentrated to a gravity of 1.40 to 1.44 and again allowed to crystallize. The material obtained from this crystallization was classed as "high-grade nitrate," and the wet salt contained 65 to 80 per cent sodium nitrate and between 6 and 10 per cent water. The mother liquor from these crystals was added to the next batch of liquor from the low-grade nitrate.

USE OF LOW-GRADE NITRATE UNSATISFACTORY.

In the making of nitric acid from this recovered nitrate it was necessary to work in the low-grade nitrate in small quantities with the high-grade nitrate or fresh purchased nitrate. Even under these conditions the amount of moisture and sodium sulphate present in the low-grade nitrate made its use unsatisfactory. When the losses were taken into consideration, as well as the cost of the additional sulphuric acid required because of the presence of the large amount of sodium sulphate in the nitrate, it was found not only more satisfactory, but actually cheaper, to use nitric instead of sulphuric acid in the neutralization of the sodium carbonate in the uranium and vanadium tanks. Under these conditions it is not necessary to crystallize out any sodium sulphate, as the amount present is small, coming from the ferrous sulphate and also the sulphuric acid used in the precipitation of the radium barium sulphate. The nitrate obtained under these conditions usually runs from 80 to 85 per cent $NaNO_3$.

STORAGE OF NITRATE SOLUTION.

According to the present arrangement, tanks *11* and *12* in the new plant (Pl. VI) are used as storage tanks for the nitrate solution from both plants, as the vanadium precipitate from both plants is filtered through filter press *18* (Pls. VI and VII) in the new plant. Partial evaporation takes place in both tanks, waste steam being used. The liquor is then pumped from the tanks into the evaporators (*43*, Pl. VI), where evaporation is carried on until a gravity of 1.4 is obtained. At this gravity crystals will usually separate out to some extent in the hot liquor, and on running the liquor into the crystallizing pans crystals are frequently found on the bottom of the evaporator.

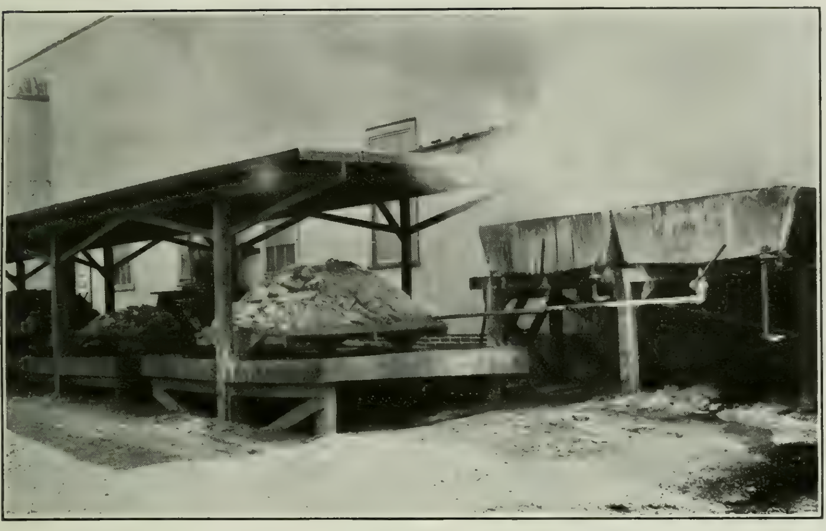
The eight crystallizing pans are divided into two groups of four, each group taking care of one day's run from both plants, so that crystallization takes place over a period of 48 hours. The mother liquor from the first crystals is pumped through a Worthington pump back into the evaporator, this pump being the same as is used to pump the liquor from the reservoir tanks into the evaporators. On the second evaporation the gravity is run to between 1.44 and 1.46, the mother liquor from these crystals being added to the next batch of fresh material.

The sodium nitrate obtained after the removal of the mother liquor is shoveled out onto the draining boards which are built over the crystallizing pans. After thorough drainage the nitrate is removed to the nitrate storage house, situated between the crystallizing pans and the nitric-acid plant.

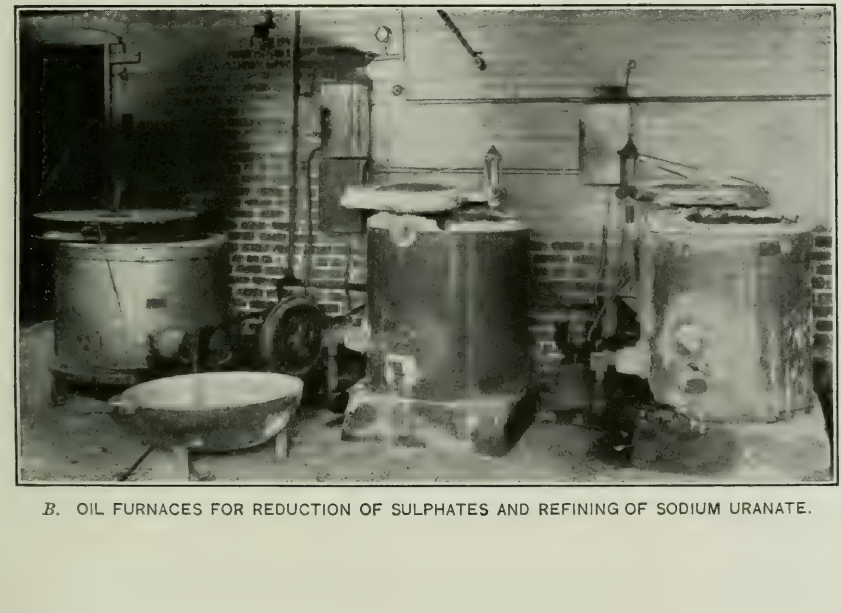
METHOD OF USING CRYSTALLIZING PANS.

The actual procedure in using the different crystallizing pans is as follows:

The mother liquor from pans *1, 2, 3,* and *4* (Pl. III), or in reverse order, is pumped into one of the evaporators as needed. After all of the mother liquor from the four pans has been introduced into the evaporator, the crystals from the previous crystallization are shoveled from the pans onto the draining boards (Pl. XI, *A*). The liquor in the evaporator is then run into pan *1* for the second crystallization. Sometimes the volume of this liquor is large enough to make the use of pan *2* also necessary. The nitrate solution, which has been more or less concentrated in the storage tanks (*11*, *12*, Pls. VI and VII), meanwhile has been further concentrated in the other evaporator. When a gravity of 1.4 is reached, the liquor is run into pans *2, 3,* and *4* for the first crystallization. The next day the same process is repeated with pans *5, 6, 7,* and *8*, the mother liquor from the second



A. EVAPORATION AND CRYSTALLIZING PANS FOR RECOVERY OF SODIUM NITRATE.



B. OIL FURNACES FOR REDUCTION OF SULPHATES AND REFINING OF SODIUM URANATE.

crystallization in each instance going back into the fresh material from the plant.

Since both plants have been running full capacity, the average weight of sodium nitrate recovered per day has been close to 4,000 pounds on the 100 per cent basis. This, of course, has varied to some extent, as the recovery has varied also. The average analysis of the nitrate during this period has been as follows:

Average composition of nitrate solution.

Constituent.	Proportion in the solution.		
	Maximum.	Minimum.	Average.
	Per cent.	*Per cent.*	*Per cent.*
Sodium nitrate	85.00	83.38	84.33
Sodium sulphate	4.80	3.99	4.39
Sodium chloride	3.96	2.32	3.16
Water	8.25	7.08	7.94

NITRIC ACID MANUFACTURE.

A plan of the nitric acid plant is shown in Plate XII. The sodium nitrate is elevated by means of the elevator *c*, and is bedded and sampled at *b*. As the composition of the nitrate varies to some extent, every day, it is necessary to make a daily analysis of the nitrate used. The charge is wheeled in wheelbarrows from *b* to the stills *d*. The bleacher and the Hart condensers are shown at *e*, the towers at *f*, and the storage pots at *g*. As the manufacture of nitric acid is more or less standardized, it is not necessary to describe it in detail in this report. The plant has produced an average of 5,250 pounds of acid per day over a period of several months, the whole of the acid averaging 63 per cent in strength.

URANIUM REFINING.

As already stated under the description of the precipitation of uranium, most of the sodium uranate that is obtained contains 7 to 9 per cent of V_2O_5 on the dry basis. It has been impossible to precipitate sodium uranate in alkaline solution containing both uranium and vanadium and not precipitate at the same time a considerable amount of vanadium with the uranium. As uranium should be as free from vanadium as possible, the economical refining of the uranium is important.

METHODS FIRST USED.

The first attempts to remove the vanadium from the sodium uranate were along the line of reprecipitation. The sodium uranate was redissolved in hot dilute sulphuric acid and sodium hydroxide added in sufficient excess to reprecipitate the uranium. It was found that one precipitation carried on in this manner reduced the amount of V_2O_5 in the sodium uranate by about 50 per cent. A second reprecipitation reduced the amount of V_2O_5 that was left in the product again to about half, so three, and sometimes even four, reprecipitations would be necessary to reduce the V_2O_5 content below 1 per cent. Such a procedure, of course, would not be commercially feasible. Consequently, it was necessary to find some other methods that would be more economical.

If sodium uranate containing vanadium is heated with somewhat concentrated nitric acid, evaporated almost to dryness and then treated with water, the larger part of the vanadium remains undissolved, but the vanadium carries considerable uranium, and the uranium still retains some of the vanadium. If more dilute acid is used and boiling continued for only a few minutes, practically all of the vanadium can be precipitated, but the precipitate still retains a considerable amount of uranium. Somewhat the same results can be obtained with hydrochloric or sulphuric acid, but with either, the precipitate of vanadium carries down considerable quantities of uranium.

RESULTS OBTAINED BY VARIOUS INVESTIGATORS.

Smith and Gibbs [a] have shown that vanadic acid can be removed from heated sodium uranate by means of hydrogen chloride, the vanadium volatilizing. Hillebrand [b] has shown that vanadium also can be partly removed in the same manner from ores. In the case of the sodium uranate, the product left behind is probably a mixture of sodium chloride, uranyl chloride, and sodium uranate. Barker [c] obtained similar results. He also removed vanadium from sodium uranate by mixing the uranate with twice its weight of ammonium chloride and enough water to make a thick paste. On heating, the vanadium may be practically completely volatilized, the amount left in the residue being reduced to as low as 0.5 per cent. The ammonium chloride at the same time converts the uranium present to ammonium uranate, which yields uranium oxide. If the temperature is too high, the amount of oxide obtained is reduced materially, as some of the oxide is converted back to sodium uranate. The best conditions are obtained when the temperature is not raised higher than is necessary to volatilize the vanadium and the ammonium chloride.

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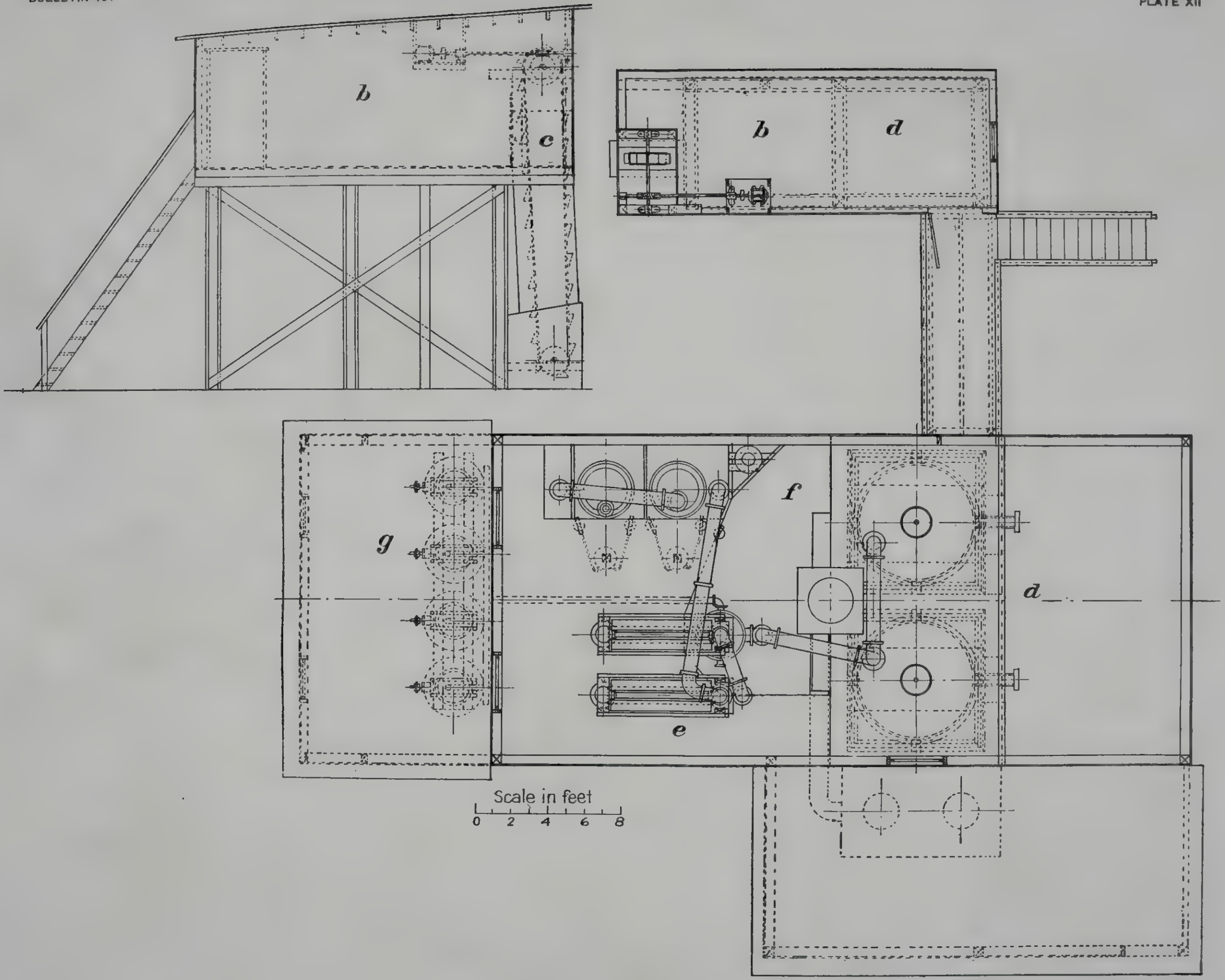
[a] Jour. Am. Chem. Soc., vol. 16, 1894, p. 578.

[b] Hillebrand, W. F., and Ransome, F. L., Carnotite and associate minerals: Bull. 262, U. S. Geol. Survey, 1905, p. 9.

[c] Barker, H. H., Unpublished thesis.


b
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8

PLAN OF NITRIC ACID PLANT.

Any of these methods might be used for the removal of the vanadium, but on a commercial scale practically all of them involve serious difficulties. The use of nitric, hydrochloric, or sulphuric acid would give excellent results, provided the precipitation between the vanadium and uranium was sharp and complete, but if all the vanadium is to be removed such a separation is practically impossible. Too much uranium goes with the vanadium, and if the loss of uranium is reduced, a considerable amount of vanadium is not separated from the uranium.

FUSION METHOD.

The authors have found, however, that the vanadium can be separated from sodium uranate cheaply and efficiently by fusion methods. If sodium uranate is heated with two to two and one-half times its weight of sodium sulphate until the whole mass is fused, and the product is afterwards broken up and leached, practically all of the vanadium goes into the solution and the uranium still remains as insoluble sodium uranate. In this manner the vanadium content of sodium uranate can be reduced from 8 or 10 per cent to less than 0.5 per cent by one treatment, practically all of the vanadium being removed if the product is sufficiently washed.

The main trouble with this method is in finding a satisfactory container for the material during fusion. Steel is slightly attacked by fused sodium sulphate, and cast iron, although standing up much better under the action of the molten material, has too low a melting point to make its use advisable for straight sodium sulphate. Although the sulphate has a melting point much lower than that of cast iron, when considerable quantities of sulphate are used it is difficult to get the center part of the mass melted before the exterior reaches the melting temperature of cast iron. Vitrified brick stands up well, and therefore a small reverberatory furnace could be used. The authors have found it more convenient, however, to add a small quantity of sodium nitrate to the sodium sulphate, in order to lower the melting point of the sulphate. If 20 to 25 per cent of sodium nitrate is added to the sodium sulphate, a melt can be readily obtained in a cast-iron pot.

USE OF OIL FURNACES.

Oil furnaces with Case burners (Pl. XI, *B*) have been used at the plant of the National Radium Institute, the pots holding 150 pounds of the mixture of sodium nitrate and sodium sulphate. To this melt is slowly added from a hopper 40 to 50 pounds of sodium uranate, with frequent stirring by means of an iron rod flattened at the end and inserted in a wooden handle. Care must be taken that effervescence does not occur too rapidly, as otherwise the pot may boil over.

After the sodium uranate has been completely added, heating must be continued for about one hour longer, in order that all of the material may be acted upon by the melt.

It is run out through a spout at the bottom of the pot into a suitable iron container, broken up, run through a ball mill, either dry or, preferably, with water, and leached with boiling water in a suitable tank. The leaching is done in tank *4* (Pls. III and IV, *B*) in the first plant, and the product pressed through filter press *33b* (Pl. IV), the filtrate running into tank *7* (Pl. III), in which the vanadium is precipitated. The sodium uranate thus obtained, provided the fusing has been carried out properly, is practically free from vanadium.

FUSION WITH SODIUM SALTS.

This procedure fitted in excellently with the main process, as sodium sulphate containing sodium nitrate was one of the by-products in the crystallizing of the sodium nitrate, and therefore purchase of the material was not necessary. Other sodium salts besides sodium sulphate, or a mixture with sodium nitrate, have a similar effect. Fused sodium hydroxide, sodium carbonate, or a mixture of sodium hydroxide and sodium carbonate, removes vanadium from sodium uranate, the sodium uranate being insoluble in a leaching process, but neither the hydroxide nor the carbonate gives as good a result as sodium sulphate. Ordinary salt, however, is just as efficient as sodium sulphate. In addition it has the advantage of not attacking cast steel, so that steel pots may be used and the salt readily melted therein. For this reason salt was substituted for the mixture of sodium sulphate and sodium nitrate at the Radium Institute.

"LIGHT" AND "DARK" SODIUM URANATE.

The sodium uranate that is obtained by this fusion method is off color. In order to obtain the light-yellow material, re-treating would be necessary. If the uranium is present as double sodium uranyl carbonate, the color of the product can be controlled without much difficulty. If acid is added to the solution until neutralization is almost complete, the precipitate that comes down is light yellow, sometimes almost white. If before neutralization is actually completed, sodium hydroxide is added until all of the uranium is precipitated, the color of the precipitate will be light yellow. The same result can be accomplished by adding acid until the solution is slightly acid, and then adding sodium hydroxide until precipitation is just complete. In order to get the dark variety of sodium uranate by direct precipitation, all that is required is to add sodium hydroxide to the solution of sodium uranyl carbonate without previous partial or complete neutralization. It is also advisable not to wash too thoroughly the sodium uranate obtained in this manner. Unless there is no objection to the presence of vanadium the precipitation of part of the vanadium along with the uranium, of course prevents the direct handling of the material in the manner described.

CONVERSION OF SODIUM URANATE INTO URANIUM OXIDE.

The conversion of sodium uranate into uranium oxide is also of interest. The first work of this kind done by the authors involved precipitation with ammonium hydroxide in order to obtain ammonium uranate, so that on ignition of the uranate U_3O_8 could be obtained. Boiling the sodium uranate with a strong solution of ammonium chloride was also tried. Some laboratory experiments were carried out on these methods before they were used in the plant, with the following results:

A 5-gram sample of dry sodium uranate was dissolved in 3 c. c. of concentrated sulphuric acid diluted with 25 c. c. of water, and the solution was poured into 25 c. c. of ammonia, the total volume being made up to 100 c. c. Excess of ammonia was expelled by boiling until rather violent bumping occurred. The yellow precipitate was filtered off and washed twice on the filter and ignited. Another sample of the same weight was boiled with 50 grams of ammonium chloride in 50 c. c. of water. The liquid was boiled for half an hour, a drop of ammonia being added from time to time to maintain an alkaline solution. The precipitate was treated as before. The weight of the residue obtained from the first experiment was 3.99 grams, and from the second 3.85 grams.

Each residue was digested with 1 c. c. of sulphuric acid in 25 c. c. of water, the weight of the residue obtained from this treatment being 2.47 grams for the ammonia-treated material and 2.71 for the other. The difference does not represent solely the amount of sodium uranate with the uranium oxide, as under the conditions at least 15 per cent of U_3O_8 is dissolved by the acid. For the final product, U_3O_8 is what is desired, and the experiments showed that by the use of a large excess of ammonium chloride a yield of 54 per cent of U_3O_8 is obtained, and of 50 per cent by digestion in ammonium sulphate in excess.

Further experiments showed that 2 parts by weight of ammonium chloride to 1 part of uranate gave practically as good a yield as when 5 parts of the chloride were used, and the yield was not very much reduced when the amount of chloride was still further decreased so that the ratio was 1.5 to 1.

EFFECT OF REDUCTION.

In the course of the experiments it was observed that in dissolving the sodium uranate in concentrated sulphuric acid and in passing from sodium uranate to the oxide a partial reduction to uranous salts took place. It was therefore thought possible that the efficiency of the conversion might be increased by reducing the sodium uranate before its precipitation as the ammonium salt. The reduction was accomplished by adding to the sulphuric acid a solution of sulphurous acid and boiling to expel the excess of sulphur dioxide. The uranium was then precipitated by ammonium hydroxide in the ordinary way. The efficiency showed a slight increase, but the difference was within the limits of experimental error.

The results of the work clearly indicated that it is difficult to completely convert sodium uranate into ammonium uranate by one treatment with ammonium chloride or ammonium sulphate, the conversion into ammonium uranate being usually somewhere around 60 per cent. In other words, a mixture of ammonium uranate and sodium uranate is obtained. On ignition the ammonium uranate is, of course converted into oxide, which remains contaminated with the unconverted sodium uranate. The latter can be leached out by dilute sulphuric acid, the preferable strength being 4 or 5 per cent. In this manner a fairly pure oxide can be obtained, which, however, usually contains traces of sodium uranate, iron, silica, and aluminum.

PLANT PROCEDURE TRIED.

The actual procedure which was finally used in experimental work in the plant was as follows:

One hundred pounds of the refined sodium uranate was dissolved in 100 pounds of 66° B. sulphuric acid diluted with 200 pounds of water. The solution took place in an earthenware pot (*34*, Pl. IV). The sodium uranate dissolved, but the majority of the iron oxide, as well as some other impurities, remained insoluble. Most of the iron was derived from the impurities in the sodium sulphate and sodium nitrate used in the fusion method for eliminating the vanadium, as already described. The iron oxide could be removed by filtration through an earthenware filter (*35*, Pl. IV) or could be run direct into the precipitation tank (*5*, Pls. III and IV, *B*), depending upon whether it was desired to eliminate the iron, and thus obtain a higher-grade product. If the solution was not filtered, the oxide finally obtained was about 87 per cent U_3O_8. If the solution was filtered at this stage, the grade of the final product could be greatly increased, reaching as high as 95 per cent.

The solution was then run into tank *5* (Pls. III, and IV, *B*), which contained about 5,000 pounds of water, and an amount of ammonia slightly in excess of that required to neutralize the acid. After 300 pounds of sodium uranate had been treated in the manner described and run into tank *5*, the liquid in this tank was boiled for about two hours. It was then filtered through press *33c* (Pl. IV), and the filtrate discarded. If this method were used continuously on a commercial scale, it would, of course, pay to treat the solution and recover the ammonia so that it could be used again.

The washed precipitate was then removed from the press, dried, and ignited in an iron pot in one of the oil furnaces in the furnace room. In this manner, the ammonium uranate was converted into oxide. As the product obtained, as already described, consisted of a mixture of uranium oxide and sodium uranate, it was treated with a 5 per cent solution of sulphuric acid, the sodium uranate dissolving along with a small amount of oxide. The solution was run into tank *5* and retreated.

SMALL-SCALE TESTS OF OTHER PROCESSES.

Although this process worked fairly well, the costs were altogether too large to justify its permanent use. Other methods were therefore sought whereby a high-grade oxide could be obtained and the vanadium eliminated at the same time, with a decrease in the cost of conversion. In other words, a method was required by which uranium oxide could be cheaply and efficiently produced from the sodium uranate without any preliminary treatment to get rid of the 7 or 8 per cent of V_2O_5 always present. Following a suggestion made to one of the authors it was found that when sodium uranate was ignited in a platinum crucible to a temperature approaching 1,500° C., a certain part of the uranate was converted into oxide. During the heating, fumes of sodium oxide were evolved, and when the product obtained was leached with water, the water was found to be strongly alkaline and contained practically all of the vanadium that was in the sodium uranate. Some experiments were tried on a semicommercial scale, a small oil furnace containing a shelf of fire-clay on which the sodium uranate was placed being used. The flame was applied not only underneath the shelf but also over it, giving a more or less reverberatory effect. A temperature approaching 1,500° C. was obtained, and a considerable amount of sodium uranate was converted into oxide, but the conversion was by no means complete. In addition, the fire clay was attacked by the semiviscous mass. The conclusion was then reached that the only possibility of success along this line was to use an electric furnace.

TESTS OF VARIOUS CRUCIBLE MATERIALS.

It was also important to find some material that would not be seriously affected by the action of the melted sodium uranate. Among others, the following were tried:

An Acheson graphite crucible brasqued with magnesite; a similar crucible brasqued with alundum; a similar crucible brasqued with 50 parts of magnesite and 50 parts of alundum; a crucible made of silicon-carbide tubing bonded with carbon, with a graphite bottom luted in place with silicon carbide and water glass, and the inside of the crucible coated with silicon carbide and water glass; a crucible similar to the last except that quartz tubing was put in with the charge.

Alundum proved to be rather unsatisfactory, as it was quickly attacked. The magnesite lining separated fairly well from the charge, but the charge was to some extent contaminated. The charge also stuck badly to the lining of silicon carbide and water glass, and the result was that practically none of these materials appeared to be satisfactory. The experiments were carried on in a resistance furnace, with a granular carbon resistor in which the crucibles, or tubes, were embedded.

In another experiment 200 grams of sodium uranate was placed in a small Acheson graphite crucible with a direct arc from a carbon rod, constituting a small Héroult type furnace. In this, the whole charge fused, and copious clouds of alkaline fumes were given off. The product was black, and the vanadium could be readily leached out when the ground material was boiled with water. Similarly an iron pot cooled with water externally was used as a container, and two electrodes made of Acheson graphite, heated the material by means of a double arc. With this equipment several pounds of a fairly satisfactory black oxide was obtained. The results of this experiment was so encouraging that work was continued along this line in the plant.

CONSTRUCTION OF EXPERIMENTAL ELECTRIC FURNACE.

The mechanical part of the experimental furnace consisted of a heavy 4-inch L-beam 10 feet long placed horizontally 8 feet from the floor, one end being embedded in the wall and the other bolted to a 3 by 4 inch wooden support embedded at its lower end in the cement floor. At the middle of this horizontal beam, two plates, or hangers, 2 feet by 4 inches by ½ inch were suspended. In the lower ends of these a 1-inch shaft carrying the sprocket wheels was placed horizontally. Over one sprocket wheel passed a chain having one end connecting with the electrodes and the other end off to one side passing over a wheel and terminating in a counterbalance approximately the same weight as the electrodes. Over the other sprocket wheel on the shaft in the central hanger passed a continuous chain about 10 feet long, running also on a sprocket wheel placed on a 1-inch shaft attached to the upright wooden support of the main horizontal L-beam. Attached to this 1-inch shaft was a 22-inch hand wheel, the turning of which raised and lowered the electrodes.

On the floor directly beneath the electrodes was placed a cement basin about 2½ feet square and 10 inches high, sloping inward toward the bottom and drained by a 2-inch pipe. For melting the sodium uranate an iron pot standing on legs was placed in the basin. The pot was cooled by water from a ring placed about 2 inches from the top and having $\frac{1}{16}$-inch holes every half inch. About 3 inches of water was allowed to back up into the basin to cool the bottom of the pot. Around the inside of the basin, stones and bricks were packed loosely about halfway up the pot to minimize danger from an explosion, if any of the molten material should be thrown out of the pot. These loose stones and bricks were kept away from the pot by a sheet-iron sheath around the pot, being enough larger to allow free play for the cooling water to run down the sides of the pot.

VOLTAGES USED.

The voltage first used was 170 volts, but after several trials the arc was found to be too heavy and to sputter too much. Other voltages ranging from 80 to 130 were tried, 130 volts proving the most satisfactory, although a 110-volt pressure was used to some extent. Leads of 600,000 circular mils about 20 feet long extended from the transformers, which were not sufficiently flexible to be connected to the electrodes, so that they were spliced to 5-foot lengths of flexible leads, $\frac{1}{2}$ inch by 2 inches in cross section, made of soft-copper strips wrapped with tape.

In order to start the arc, it was found that the best method was to use a piece of uranium oxide from a previous charge, which was heated in an oil blast to bright redness and placed beneath and in contact with the electrodes. Such material is sufficiently conducting to melt and form the desired pool.

MELTING POTS USED.

The preliminary work was done in cast-iron pots, which, however, did not stand up under the treatment, and usually, after one or two runs, were melted through at some point. In order to make the pots last longer, a coating of fire clay on the inside was tried, magnesite being afterward substituted. The molten material, however, attacked, and to some extent dissolved both the fire clay and the magnesite; consequently, their use was abandoned. Finally, the plan already described was adopted, namely, the use of a heavy pot made of $\frac{3}{8}$-inch boiler plate 14 inches in diameter and 10 inches on the side, with a round bottom, dipped 2 inches, and standing on legs, so that the lowest point of the bottom stood half an inch from a level floor. The pot was riveted and worked well when it was cooled by a stream of water from a circular pipe that surrounded it, as already described. The pot would hold about 160 to 175 pounds of product, but was unwieldy to remove and dump, so ladling was resorted to at intervals. This resulted in a yellow coating appearing on the material, which was probably re-formed sodium uranate, increasing the percentage of this impurity in the product. In order to eliminate this trouble as much as possible, a second pot was made, and after the charge had cooled the pot with contents was removed and the second one substituted.

PRODUCT OBTAINED.

The product finally obtained consisted of UO_2, containing small traces of undecomposed sodium uranate, especially on the top and sides of the charge, and also some Na_2O that had not been vaporized. After the product had been put through a ball mill and leached with water, the filtrate contained most of the vanadium that had been in the original sodium uranate, and this was recovered in the usual way. The leaching also washed out the soda which was present.

In order to eliminate the trace of sodium uranate, it was necessary to wash with dilute sulphuric acid, sodium uranate being soluble in a 4 or 5 per cent acid, whilst the oxide is not. Uranium oxide (UO_2) is much less soluble not only in sulphuric acid but also in hydrochloric acid than U_3O_8, the amount of oxide going into solution with this treatment being small.

EXPLOSIONS IN ELECTRIC FURNACE.

Explosions in the melt, which quickly developed in connection with the use of the electric furnace, finally forced its abandonment. The explosions were of two distinct types—one like a sharp pistol crack, the other of full, round, cannon-boom character. The first frequently occurred alone, but the latter was always preceded by a sharp explosion. The sharp explosions evidently came from the melt, as they always threw molten material from the pot. At times the furnace could be operated for a considerable period smoothly and satisfactorily, when suddenly loud "cracks" would be heard, followed by molten material being thrown in all directions. Sometimes these cracking explosions would occur every 15 or 20 minutes. At first the authors were rather inclined to believe that the explosions were due to nitrate left in the sodium uranate, but later experiments with material washed perfectly free from nitrate gave the same results. Two or three of the explosions were violent enough to tear the hood from the bolts, break the "transite" asbestos boards, and throw the bricks out of the cement basin.

The possibility of the "booming" explosions being due to an explosion of carbon monoxide formed from the electrodes was investigated. Samples of gas were taken from just over the pot at several intervals and analyzed. In each sample mere traces of carbon monoxide or hydrogen were present; consequently, this explanation had to be abandoned. In addition, the draft through the hood was so excellent that there was no possibility of an accumulation of a sufficient amount of gas to cause the explosions. It is possible that they were caused by the sudden oxidation of Na or Na_2O, but the authors were unable, under the conditions, to establish that theory. Although the operators were well protected by screens, operation of the furnace finally became so dangerous that its use was abandoned and the furnace was dismantled. Further work along this line, however, should be of value.

COST OF TREATMENT WITH ELECTRIC FURNACE.

Only a rough approximation of the cost of such treatment can be given, as the work was of purely experimental character. If the explosions could be eliminated, somewhere around 75 pounds of finished product per hour could be obtained with a pressure of about 110 volts and a current of about 600 amperes or about 65 kilowatt-hours. The electrodes wore away at the rate of about 3 inches per 100 pounds of output, and as only about one-half or less of a 30-inch electrode could be utilized, two electrodes would be needed for every 400 to 500 pounds of product.

After the abandonment of the electric furnace, experimental work was continued in an entirely new direction, and finally a method was evolved that appears satisfactory. The details of this method will be described in a later report of the Bureau of Mines.

CHAPTER IV. RADIUM REFINING.

REFINING IN THE PLANT.

The first treatment of the radium-barium sulphates is of great importance, as the whole capacity of the plant, as far as the radium goes, depends upon this first treatment. If the sulphates can not be handled as rapidly as produced, the actual amount of radium refined each year must necessarily be much below the capacity of the plant itself. The tediousness of the process used by Haitinger and Ulrich (see p. 20) can be readily appreciated on reading the account of their work. In order to produce 5 to 10 grams of radium metal per year, it is absolutely necessary to have shorter methods of handling the sulphates than were used in the early days of radium refining.

The first step in this direction is to obtain a high-grade sulphate, as sulphates containing a considerable amount of silica and other impurities are not nearly as readily treated as those that are comparatively pure. Therefore, any process for the treatment of carnotite or pitchblende that involves the precipitation of a high-grade, clean sulphate has a great advantage over other processes involving the precipitation of the sulphate along with silica or allowing the sulphate to remain in the residue with silica and other impurities. This is one of the advantages possessed by the process described in this report. As a rule, the sulphates obtained contain at least 85 per cent $BaSO_4$, and in much of the product the proportion of barium sulphate present is as high as 90 per cent. The proportion of radium in these sulphates has averaged about 1 milligram of radium metal per kilogram of total weight.

OLD METHOD OF TREATING RADIUM-BARIUM SULPHATES.

The old method of boiling the sulphates with a solution of sodium carbonate in order to obtain radium carbonate and sodium sulphate is one that can be applied to any radium barium sulphate. It involves, however, considerable labor and much filtering and washing, as the radium-barium carbonate obtained must be washed completely free from traces of sulphate. The carbonate is then dissolved in chemically pure hydrochloric acid and filtered, and any insoluble material is worked up with the next batch of sulphate. If three parts of sodium carbonate dissolved in water is boiled with one part of radium-barium sulphate, a considerable part of the sulphate is converted into carbonate at one treatment. It is claimed that this conversion can be improved if the heating is done under pressure in an iron tank, although the authors have not tried this method. Any method, however, that will shorten this somewhat tedious process should be welcomed.

RESULTS OF EBLER'S EXPERIMENTS.

The results obtained by Ebler[a] are suggestive. In his experiments he used two sulphates, one low grade and the other high grade. The low-grade sulphate contained 37.1 per cent barium sulphate, 21.8 per cent silica, and 23.9 per cent total sulphate, with traces of vanadium, iron, aluminum, etc. The radium content was only 0.032 milligram per kilogram. The analysis of the high-grade sulphate was as follows:

Results of analysis of high-grade sulphate.

	Per cent.
$BaSO_4$	65.7
$PbSO_4$	4.5
$CaSO_4$	19.3
$FeSO_4$	1.4
SiO_2	5.0
Ra (metal) milligram per kilogram	0.35

On heating these sulphates with carbon to a bright red heat for two to four hours he obtained a 32 per cent reduction with the low-grade and a 68 per cent reduction with the high-grade sulphate.

With calcium carbide the following reaction takes place:

$$MeSO_4+4CaC_2=4CaO+MeS+8C$$

The temperature and time of heating was the same as for carbon. With the low-grade sulphate he obtained an 83 per cent reduction and with the high-grade sulphate a 70 per cent reduction, showing an improvement in carbon with the low grade, but not with the high grade.

With calcium hydride a spontaneous reaction takes place as follows:

$$MeSO_4+4CaH_2=MeS+4CaO+4H_2$$

The reduction with the low-grade material was 75 per cent, and with the high grade 80.5 per cent.

Ebler also tried a mixture of calcium hydride and carbide. The low-grade sulphate required three parts of the former to one of the latter to produce a 64 per cent reduction. The high-grade sulphate gave a 60 per cent reduction with one part of hydride to two parts of carbide.

In general, he found that the crude sulphate was better reduced by the more vigorous reducing agent. Although the reactions with calcium hydride and carbide are immediate and spontaneous, the cost and the difficulty of obtaining calcium hydride make the desirability of their use doubtful.

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[a] Ztschr. angew. Chem., vol. 28, pp. 25–48.

REDUCTION OF BARIUM SULPHATE BY COAL GAS IN AN ELECTRIC FURNACE.

It is a well-known fact that barium sulphate can be reduced by heating in a current of coal gas. This method promised good results, although others had tried it and had reported failure without giving details. As temperature control within reasonably narrow limits was necessary in order to get reduction, and at the same time to get the material in a nonclinkering condition so that it could be readily removed from the tube in which it was heated, the use of an electric furnace seemed more desirable than heating by coal, oil, or gas.

The reduction chamber of the electric furnace consisted of a cast-iron tube 5 feet long and 6 inches in internal diameter. Around this was wound 120 feet of No. 21 nichrome ribbon, the insulation being asbestos cloth and a double layer of mica, the pieces being 4 inches by 5 inches in size.

Reduction begins at 575° to 600° C., the actual working temperature being 725° to 740° C. For raising the temperature a current of 40 to 50 amperes was required, and for maintaining it during the reduction, 15 to 20 amperes from a 220-volt circuit. The gas consumption averaged 200 to 300 cubic feet per run on 25 to 28 pounds of sulphate.

The heat of reduction was positive at high temperatures, producing reaction clinkers, some of which were friable and some glassy and hard to break. The formation of the clinkers did not seem to affect the reduction, which varied from 75 to 90 per cent.

The main advantage of a reduction with coal gas lies in the fact that no foreign material is introduced. The principal disadvantage is the difficulty of maintaining the insulation owing to the deterioration of the mica. Silicon-carbide tubes were also tried in the electric furnace instead of cast-iron tubes without success. As a rule, after 8 or 12 runs a tube would have to be rewound and the insulation renewed, and during reduction the furnace needed constant attention in order to maintain the correct temperature. The iron tube was also gradually attacked by the charge.

A constant-feed furnace of much smaller size, having an alundum tube, was also built. The difficulty was in getting a proper feed through the furnace and a sufficiently high reduction. When the tube got hot it became sticky, and the rate at which the sulphate went through could not be controlled.

REDUCTION WITH CHARCOAL.

While the work was being done with the electric furnace, the reduction of radium-barium sulphates with charcoal was tried. This was done by mixing the sulphate with about one-fifth its weight of powdered charcoal and heating for 7 or 8 hours in a graphite crucible in an oil furnace, the temperature being about 800° C. Reduction takes place readily, according to the equation $BaSO_4 + 4C = BaS + 4CO$, with carbon monoxide burning at the spout of the crucible. When the evolution of gas has stopped, the crucible is allowed to cool with the lid on, and the radium-barium sulphide is removed and broken up. Under such conditions, with a sulphate reasonably free from silica, it is usual to get a 90 per cent reduction of the sulphate to sulphide, the ratio of the reduction of the radium being the same. The sulphide is then dissolved in dilute chemically pure hydrochloric acid. This step should be performed out-of-doors or with a hood having a good draft, as the evolution of hydrogen sulphide, of course, is large. The gas also catches fire spontaneously at times, owing to the possible formation of small quantities of phosphides, although it is difficult to see how these could be formed under the conditions. If the work is conducted in open vessels in the open air this danger is minimized. The residue obtained on filtration consists of undecomposed radium barium sulphate, a small amount of charcoal, and some silica. The amount of radium in this residue is usually about the same as that in the original sulphate. The residues are stored and re-treated in the same manner, although filtering them after leaching with acid is more difficult than filtering a sulphide obtained from an original sulphate.

After the re-treatment of these residues, a third residue is, of course, also obtained. There is a tendency for the accumulation of lead in the second and third residues, especially the latter, and, therefore, it is better to fuse the third residue with sodium carbonate than to reduce it once more with carbon in the usual way. After fusion, during which most of the lead is eliminated, the material is thoroughly washed and dissolved in chemically pure hydrochloric acid. As the weight of the second residue is only 1 to 2 per cent of that of the original radium barium sulphate treated, it is necessary to carry out this treatment only once or twice a year.

The reduction with carbon is the method that has been used almost exclusively at the plant of the National Radium Institute. An oil furnace (*23*, Pl. III) holding three No. 100 graphite crucibles handles all of the sulphate made in the plant, the furnace being used only every other day. The actual amount of charcoal required is a little more than one-fifth the weight of the sulphate treated. The charcoal and sulphate are ground in one or two small ball mills (*66*, fig. 2), a short piece of 1-inch steel rod being placed in each mill instead of balls. This treatment for 10 or 15 minutes is sufficient to intimately mix the sulphate and the charcoal. The ground material is then carefully removed from the ball mill and is placed in the crucibles, which are then transported to the furnace room.

TREATMENT OF SULPHIDE.

After reduction, the sulphide is ground in a similar manner in the other mill and is then leached with moderately dilute chemically pure hydrochloric acid in an earthenware pot placed just outside of the building. No particular precautions are necessary to prevent oxidation of sulphide to sulphate. If such oxidation does take place, the amount of radium and barium precipitated will be proportionate to the relative quantities of these elements present—roughly, 1 part per million. The material in the pot is then transported in crocks to an earthenware suction filter, and the filtrate, which consists of an almost saturated solution of radium-barium chloride, is ready for fractionation. In actual practice it has been customary to use an amount of acid that will not be saturated with barium chloride when hot, but will be almost saturated when cold. This precaution reduces the boiling afterwards required to get the first batch of crystals.

EQUIPMENT FOR FRACTIONATION.

The actual arrangement for fractionation as indicated in figures 2 and 3 is not the arrangement that has been used up to the time of writing (September, 1915), but is what will be used after additional acid-proof ware has been received from France. In the past it has been necessary to use an inadequate equipment, so that the refining capacity has been less than that of the rest of the plant. With the equipment shown in figures 1 and 2, however, it will be possible to refine considerably more than the total output of the plant, now about 400 milligrams per month.

PROCEDURE IN FRACTIONATION.

The method of treatment with this new equipment is to be as follows:

The radium-barium sulphides are dissolved in an earthenware pot, *63* (figs. 2 and 3). The solution and the insoluble material are run onto the upper part of a suction filter, *64*. After filtration and washing, the liquor is run into the upper steam-jacketed vessels, *65*. These vessels are made of silica-lined acid-proof ware, as previously described (p. 44), the upper three each having a capacity of 250 liters and the lower two each having a capacity of 200 liters. The evaporators are covered by two wooden hoods, in the flue of which is placed a small steam jet to produce a sufficient draft to carry off the hydrogen chloride fumes. The barium chloride solution in the first evaporator, *65*, is then so concentrated that on cooling one-half of the barium chloride crystallizes out. The liquor is siphoned into evaporator *65a* and the process repeated, one-half of the remaining barium chloride being allowed to crystallize. This procedure can be continued all the way down the series, or a fresh batch of liquor may be introduced into *65a* after the crystals have been removed.

The system may be established in several ways, either by adding fresh material to *65* each day and gradually working the mother liquors down the evaporators to the bottom of the series, or by crystallizing the first batch of liquor introduced into *65* all the way down the series before the introduction of fresh material. Whichever method is used, the procedure afterwards adopted is the same. Half of the barium chloride in evaporator *65d* is crystallized out and removed from the mother liquor. This liquor should then be discarded entirely. After the crystals have been removed from the evaporator, the liquor obtained from a similar crystallization in *65c* is siphoned into *65d*. The liquor from a similar crystallization is then siphoned from *65b* into *65c*, and the crystals from *65d* are dissolved with this liquor in *65c*. In other words, the crystals from each evaporator ascend, and the mother liquors at the same time descend, the crystals from a given evaporator being dissolved in the liquor from the second evaporator above.

For example, the crystals from *65d* will be dissolved in the liquor from *65b* in the evaporator *65c*, with the addition of the minimum amount of water required, the crystals from *65c* will meet the liquor from *65a* in *65b*, and will be dissolved in this liquor, and so on up the series. The new material is always introduced into *65*. The crystals obtained from *65* are then refractionated twice in smaller pots (*62*) of about 80-liter capacity, the liquor from the first crystallization coming back into *65* in the same manner as already described. Evaporator *65*, therefore, may be considered as the "zero" pot, with the barium going in one direction and the radium in the other. After the second recrystallization in the smaller pots, the material is ready to go to the laboratory, the ratio of radium to barium varying from 4 to 10 parts per million. The whole method is more fully described on pages 76–86.

The crystallization factor of hydrochloric-acid solution is about 1.5 to 1.6; that is to say, if 50 per cent of the barium chloride is removed, there will be 50 per cent more radium in the crystals removed than in the liquor left behind. Owing to lack of equipment only two "minus" crystallizations have in the past been given in acid solution. The average radium content of the liquor thus obtained has been too high to discard, averaging during the past few months, 0.0679 milligram of radium per liter of solution, or a ratio of radium to barium of 187.5 parts per billion. With three, or even two more "minus" crystallizations, as planned, the radium content of this material could readily be reduced so that the final liquor could be discarded.

In actual practice up to September, 1915, this solution has been neutralized with ammonia, preferably filtered, and fractionated in the manner already described, in a series of seven bathtubs shown at *52* in Plate VII. The head batch of crystals is then put back at a suitable point in the acid crystallizing system and the tailings either discarded or used as barium chloride solution for the precipitation of fresh batches of barium sulphate in the plant. During the past few months, the average radium content of the tailings discarded, or used as described, has been 29 parts per billion. Ordinarily, material having 40, or even 50, parts of radium per billion might well be discarded.

At all necessary stages in the fractionation, samples are taken for the determination of radium, so that a check may be kept on the progress of the work.

LABORATORY REFINING.

Radium of any desired degree of purity may be obtained by fractional crystallization of the barium solution, first as chloride and later as bromide. The radium continues to be enriched in the crystal fractions and impoverished in the successive mother liquors, as already described.

The salts of most metals, such as iron, aluminum, and vanadium, that may occur with the radium-barium salt as impurities, pass into the mother liquors, and give no difficulty in the enriching radium fractions. Lead is an exception, however, and requires special treatment. Where barium (radium) sulphide, after reduction from sulphate is dissolved in hydrochloric acid solution with copious evolution of hydrogen sulphide (see p. 74), one might expect the almost complete removal of the lead content. This by no means occurs, no matter what precautions are taken in the way of final acid concentration or other conditions, such as have been prescribed by other authors.[a] The treatment necessary to remove all lead and the reasons for its seemingly abnormal action are discussed in a subsequent section.

Figure 5 shows the steps of the concentration system employed in the laboratory.

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[a] Ebler, Erich, and Bender, W., Sitzb. Heidelberger Akad. Wiss., Abt. A, Abh. 18, pp. 6, 7; Ztschr. anorg. Chem., vol. 83, 1913, pp. 152-153.

TREATMENT OF CHLORIDES.

The crude barium (radium) chloride received from the plant, containing 4 to 10 parts of radium element per million, is dissolved in water in large porcelain dishes (Pl. XIII, *A*), and hydrochloric acid is added to precipitate as much lead as possible. After the solution has stood over night, it is filtered to remove lead chloride and whatever carbon and barium sulphate may have escaped previous filtration. For this purpose a Schleicher & Schüll 50-cm. folding filter is used repeatedly (10 to 12 times) until clogged, when it is washed,

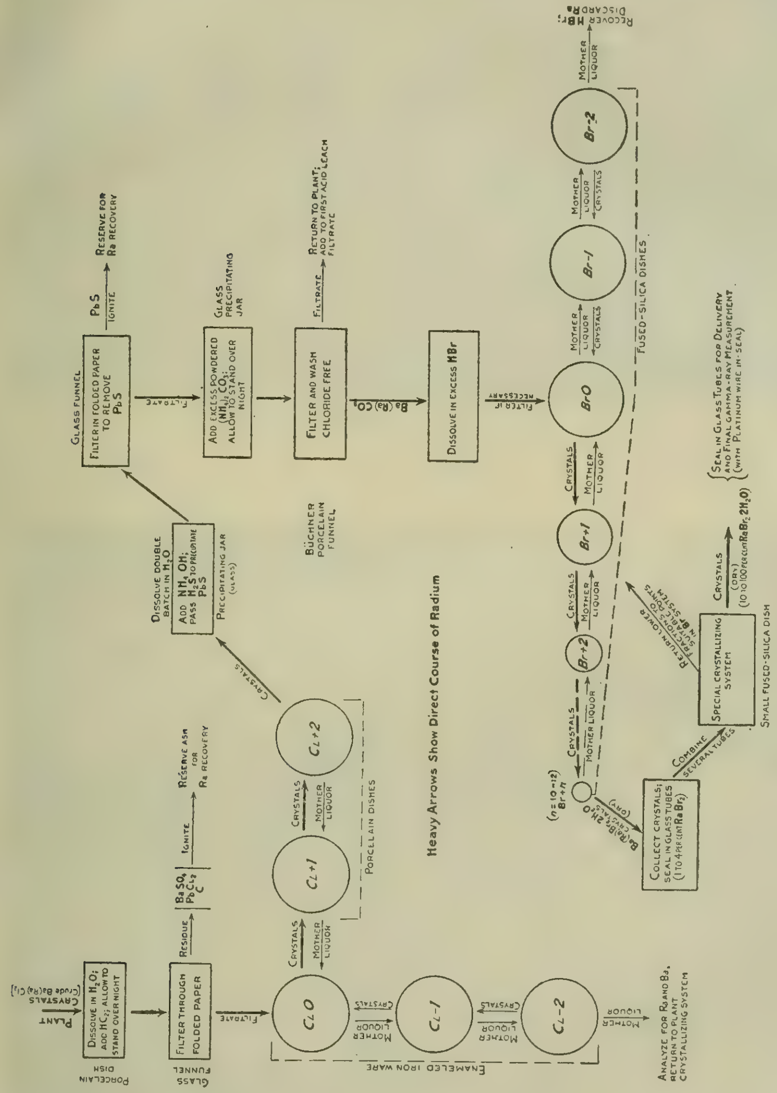

Plant
Crystals [Crude Ba(Ra) Cl₂]
Dissolve in H₂O; add HCl; allow to stand over night
Porcelain dish
Filter through folded paper
Glass funnel
Filtrate
Residue
BaSO₄ PbCl₂ C
Ignite
Reserve ash for Ra recovery
Cl 0
Cl -1
Cl -2
Cl +1
Cl +2
Crystals
Mother liquor
Enameled iron ware
Porcelain dishes
Analyze for Ra and Ba, return to plant crystallizing system
Crystals
Dissolve double batch in H₂O
Add NH₄OH; pass H₂S to precipitate PbS
Precipitating jar (glass)
Glass funnel
Filter in folded paper to remove PbS
PbS
Ignite
Reserve for Ra recovery
Filtrate
Add excess powdered (NH₄)₂CO₃; allow to stand over night
Glass precipitating jar
Filter and wash chloride free
Büchner porcelain funnel
Filtrate
Return to plant; add to first acid leach filtrate
Ba(Ra)CO₃
Dissolve in excess HBr
Filter if necessary
Heavy Arrows Show Direct Course of Radium
Br-0
Br-1
Br-2
Br+1
Br+2
Br+n
(n=10-12)
Mother liquor
Recover HBr; discard Ra
Fused-silica dishes
Ba-RaBr₂·2H₂O crystals (dry)
Collect crystals; seal in glass tubes (1 to 4 per cent RaBr₂)
Combine several tubes
Special crystallizing system
Small fused-silica dish
Return lower fractions to system
Crystals (dry) (10 to 100 per cent RaBr₂·2H₂O)
Seal in glass tubes for delivery and final gamma-ray measurement (with platinum wire in seal)

FIGURE 5.—Diagram of laboratory crystallizing system.

dried, and ignited together with the residue, which is held for treatment to recover the radium.

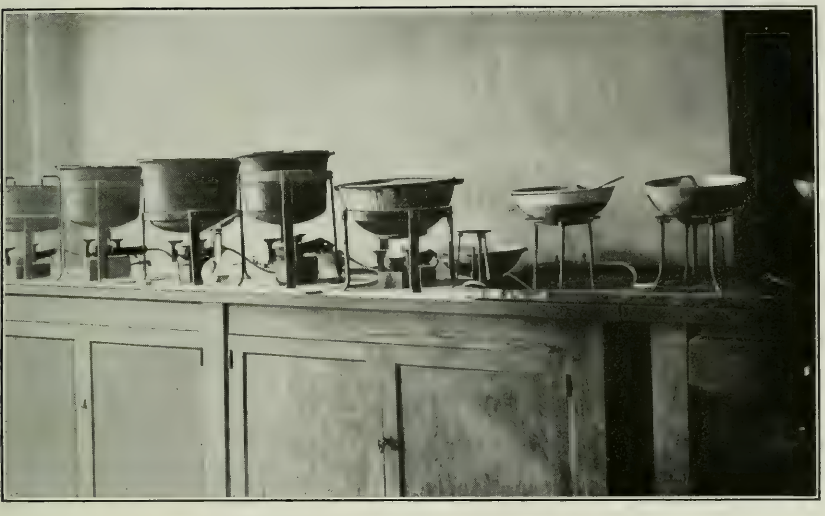
The filter ash and residue, after the passage of about 1,500 milligrams of radium element, weighed 9.5 kilograms and contained 37 milligrams of radium, or about 2.5 per cent of the total put through. The residue would therefore contain about 4 milligrams of radium per kilogram, being considerably richer in radium than the original first sulphates. During part of the operations, however, the residue ran as low as 1 milligram per kilogram (about the same as the original first sulphates), which shows that thorough washing can reduce the radium ratio at this point to that in the original insoluble material.

The filtrate is made up to an 8-liter volume, and, after a sample of 0.01 c. c. has been taken for analysis, the filtrate is introduced into the chloride crystallizing system in the vessel designated *Cl0* in figure 5. The vessels used for *Cl0*, *Cl−1*, and *Cl−2* (Pl. XIII, *A*) are all cast-iron ware lined with silica and were obtained from the Danto-Rogeat Co., of Lyons, France. At the time of writing (September, 1915) they have withstood continuously for 9 months hydrochloric-acid solutions which were boiled for several hours daily and yet show little or no deterioration. The pots contain, in the order named above, 16.6, 13.6, and 10 liters, and each is suited to handling about 2½ to 3 kilograms of barium chloride in one daily crystallization. The pots are mounted on iron-ring tripods and heated with perforated-cap gas burners 5 inches in diameter (see Pl. XIII, *A*).

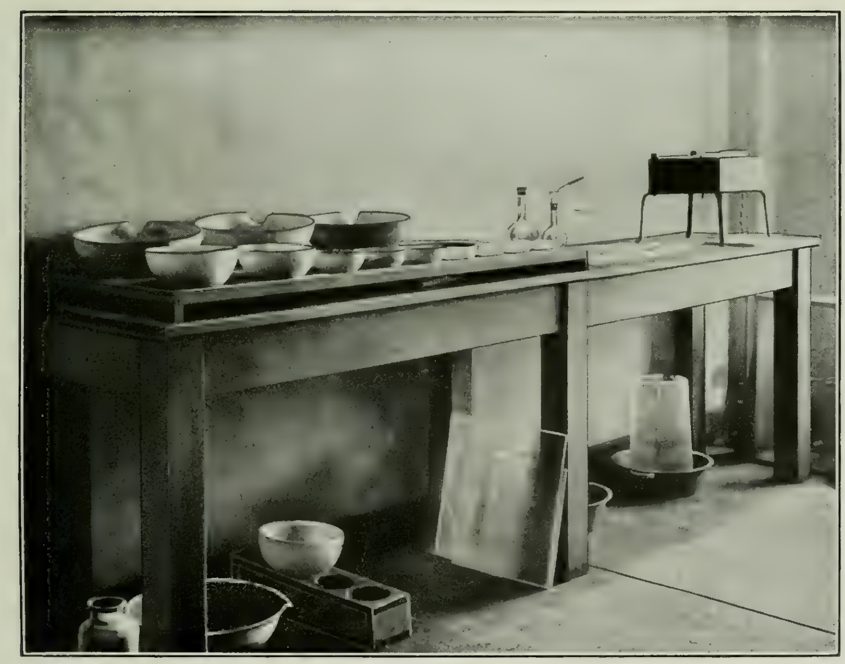
As the factor of enrichment of radium chloride from barium chloride and also of radium bromide from barium bromide is more favorable in acid than in neutral solutions, a fair acid concentration is maintained throughout the chloride and bromide systems.

As indicated in figure 5 in both systems the crystals moving forward are combined with mother liquors moving backward from pots two places removed from each other in the system. Another advantageous feature of the procedure employed consists in introducing the new material, not into terminal but into intermediate vessels, so that the system may be shortened or lengthened at either end without disturbing the rest of the system. For vessels *+1* and *+2* in the chloride system either porcelain or fused silica vessels may be conveniently used.

The mother liquor from *Cl−2* is collected in 100-liter lots, which are analyzed for radium and barium before being returned to the crystallizing system at the plant. The solutions, which are saturated with barium chloride, contain 0.16 to 0.32 gram of barium chloride per cubic centimeter, the exact quantity depending upon the degree of acidity maintained, and have varied in radium content from



A. LABORATORY CRYSTALLIZING SYSTEM FOR CHLORIDES.



B. LABORATORY CRYSTALLIZING SYSTEM FOR BROMIDES.

0.00001 to 0.00020 gram of radium per liter, the exact content depending on the quantity of radium accumulated in the system and also the acidity. The total quantity of radium thus returned to the plant out of 1,500 milligrams put into the system was 60 milligrams, or about 4 per cent.

The chloride crystals from *Cl+2* are dissolved in water without acid, and the solution from two daily batches is brought into a large glass precipitating jar 16 inches high and 8 inches in diameter and made slightly ammoniacal. Hydrogen sulphide is passed in until the precipitation of lead is complete as lead sulphide. This sulphide is filtered and collected according to the procedure for lead chloride and barium sulphate already described, and analyzed. The amount of lead sulphide thus collected during the treatment of 1,500 milligrams of radium was 700 grams, which contained 3 milligrams of radium or 0.2 per cent of the total radium involved. The lead sulphide is stored for treatment to recover the radium. Some lead sulphide was collected, after sulphuric acid free from lead had been used at the plant, in order to preserve a sample of lead coming exclusively from a uranium mineral.

REMOVAL OF LEAD.

The difficulty of removing lead has already been mentioned. Attempts to precipitate it as sulphide even from slightly acid solution usually result in obtaining an orange-red precipitate, which is a sulphochloride of composition $(PbS)_x.PbCl_2$, and far more soluble in acid than lead sulphide; hence complete precipitation of the lead is possible only in ammoniacal solution. Explanation of this action is to be sought in the high concentration of barium chloride in the solution producing such a high concentration of Cl' ions that the dissociation $PbCl_2 \rightleftarrows PbCl^+ + Cl' \rightleftarrows Pb^{++} + 2Cl'$ is almost entirely arrested at the intermediate step. The absence of Pb^{++} ions and the readiness of Pb_2Cl_2S to form according to the equation $2PbCl^+ + S'' = Pb_2Cl_2S$, explains the impossibility of obtaining lead sulphide. Precipitation of Pb_2Cl_2S is only partial so far as lead is concerned and does not take place unless the acid concentration is low. Complete removal of lead as normal lead sulphide is readily accomplished, however, by passing hydrogen sulphide in ammoniacal solution. The loss of radium here has already been shown to be only 0.2 per cent.

CONVERSION TO BROMIDE.

Into the filtrate from the lead precipitate powdered ammonium carbonate is introduced gradually with vigorous stirring until all the barium has been precipitated as carbonate. Where a slight excess of reagent is added, the whole is allowed to stand over night for the settling of the barium carbonate and the thorough precipitation of the radium carbonate. The supernatant solution is siphoned off as far as possible, and the rest goes to a 9-inch Büchner funnel, where it is filtered and washed several times with suction. The filtrate, together with the wash water, designated "laboratory carbonate liquor," is stored in 50-liter lots and returned into the acid leach liquor at the plant to recover radium and assist in neutralization. The amount of radium in the liquor is surprisingly low, usually 0.001 to 0.003 milligrams per liter, and out of 1,500 milligrams of radium only 6.4 milligrams, or 0.4 per cent, remained in this liquor. In most lots the amount was much lower than this average.

TREATMENT OF BROMIDES.

By inverting the Büchner funnel the barium (radium) carbonate precipitate is removed, and after being separated from the filter paper is dissolved in chemically pure hydrobromic acid (20 to 35 per cent) in the precipitating jar already used. The Büchner funnel and the filter paper are also washed with 1 to 1 hydrobromic acid. If necessary, this solution is again filtered and washed through a Büchner funnel and then introduced directly into the *Br0* vessel.

All the vessels used in the bromide crystallizing system (Pl. XIII, *B*) are of fused silica ware, which can be more safely heated by free flame than porcelain and the solution in silica ware "crawls" less. For *Br0* the 12-inch or 15-inch dish is convenient; for *Br−1* and *Br−2* the 12-inch dish is sufficient, and the sizes fall off rapidly in the plus direction to the smallest silica dishes obtainable.

The degree of acidity to be maintained both in the chloride and bromide crystallizing systems can not be stated definitely, as it depends on operating conditions and must be left somewhat to the judgment of the operator. In general, it may be stated that the acid concentration should be maintained as high as consistent with the size of the crystal crop to be obtained and the quantity of acid fumes that can be conveniently liberated.

The silica vessels in the bromide system are heated on tripods with bare gas flames until the richer fractions are reached, when the evaporation is carried out on an electrically heated water bath in which only distilled water is used, which is shielded from the heating coils by a block-tin protector. In case of an accidental loss of radium solution into the bath, all the water can be drawn off and returned into the system just before the treatment with hydrogen sulphide.

The evaporation required to obtain a suitable batch of crystals may be generally regulated by concentrating the solution until vigorous fanning just begins to cause the formation of crystals on the surface of the hot solution. Of course, the higher the acid concentration the more generous the crystal batch will be. All vessels in the chloride system are allowed to cool over night, so that only one crystallization a day is made in each vessel in this system. In the bromide series, in which the vessels are smaller, cooling and crystallization proceed rapidly enough to permit several batches being put through in a day if desired. In warm weather the use of an ice box to contain the vessels of the bromide system facilitates operation. The vessels of the bromide system, when not being heated, are kept in order on a board with holes of sizes suited to the sizes of the various dishes. (Pl. XIII, *B*.)

The barium-chloride crystals invariably form a mat on the bottom of a vessel, from which the mother liquor is drained with some difficulty, whereas the bromide crystals form in heavy individual needles, from which the mother liquor is poured off clean with great ease. Only when the bromide system is disturbed by the presence of lead or chloride salts or when it contains too little acid do the bromide crystals fail to form in their characteristic habit. Both disturbing influences should be carefully avoided, as radium concentration is at once retarded if the bromide crystals do not retain their type.

Owing to the high factor of enrichment as bromide, the radium content of the mother liquor from *Br–2* is extremely low. Out of about 1,400 milligrams of radium treated in the bromide system, only 3 milligrams, or 0.2 per cent, went back into this final bromide liquor. In four out of six lots the radium content was only 20 to 30 parts per billion of salt. As it is not profitable to recover radium at a concentration below 40 parts per billion parts of barium salt, the liquors were treated for the recovery of hydrobromic acid only. In the two lots exceeding this concentration the barium-radium sulphate obtained in the acid recovery was stored, to be handled as second sulphates.

The method of recovering hydrobromic acid from the final bromide liquor just mentioned consists in adding a slight excess of sulphuric acid to precipitate all barium, then in adding a slight excess of the original barium-bromide liquor to remove any excess of sulphate, filtering on a large earthenware Büchner funnel, and distilling off hydrobromic acid from the filtrate, a large round-bottomed glass flask and a glass condenser being used. The distillation is repeated until at least a 20 per cent acid is obtained.

NUMBER OF FRACTIONS EMPLOYED.

The number of fractions employed in the plus direction in the bromide system varies somewhat with conditions, 10 to 12 being the usual number. The crystallization is conducted in such a way that the barium (radium) bromide collected in the final fraction should not fall below 1 per cent of radium bromide, and sometimes is as high as 4 per cent. The total weight of the fraction should be 1 to 2 grams. The factor of concentration for each step in the acid bromide system is about 2 to 2.2, and in the acid chloride system about 1.5 to 1.6.

The procedure in collecting the final fraction is as follows: The mother liquor having been poured back, the crystals are dried in the silica crystallizing dish, first on the steam bath, and finally in an air-drying oven at 105° to 110° C. until thoroughly dry. The crystals are then collected in a previously-weighed glass tube sealed at one end, 4 to 6 millimeters in internal diameter, and of sufficient length to contain the salt and permit the other end to be sealed with the blast. The total weight of salt is determined by weighing the sealed tube and contents together with the detached end. The salt is kept stored in the tube, and gamma-ray measurements of the radium content are made at intervals of a few days until the determination is thoroughly established. When a number of tubes have been collected, they are opened and the contents combined for further fractionation.

In opening tubes that have been closed for several weeks, care must be taken that the contents shall not be scattered by the release of gas that may have been generated by the chemical action of the alpha rays, especially if the salt was not thoroughly dried when placed in the tubes. Two precautions may be taken—one end may be drawn out to a capillary, which may be opened first, thus relieving the pressure; or a scratch may be made near one end, which may then be inserted well into a beaker lying horizontally and the tube opened by a hot piece of glass applied to the scratch. If a capillary end is provided, it is preferable to have this so narrow that the salt crystals can not enter and the salt will remain confined in a definite length of tube, one not too great for accurate gamma-ray measurements. It is also desirable that the drying and sealing of a tube shall follow crystallization as promptly as possible in order to furnish a definite zero point from which the accumulation of gamma radiation may be dated. This detail is more fully discussed in a subsequent description of measurements (p. 89).

PROCEDURE IN HIGHER FRACTIONATION.

After the collection and measurement of the salt in a sufficient number of tubes (usually 10 to 20), the higher fractionation may be commenced. If the percentage of radium is approximately the same in all tubes, they may be combined into one solution; if not, two or three solutions are made, which later fall into the crystallization series in their proper places.

As a guide for procedure in making this special fractionation, it has been found convenient to assume a concentration factor of 2.0 for the radium enrichment, which means briefly that if one-half of the salt is crystallized from a given fraction, two-thirds of the radium is contained in the crystals and one-third in the mother liquor. The advance fractions are then made and the lower ones recombined as suggested by this factor until it is thought that the desired products have been attained, when the crystals are collected and sealed as already described for the lower-grade salt. If the products prove on measurement not to have the desired percentage of radium, the tubes are opened again and either the salts are suitably recombined, or possibly further fractionation is carried out.

As regards the higher grade salts, one additional precaution is observed in sealing the tubes, namely, a small platinum wire is sealed through one end of the tube to conduct away the unipolar charge that may collect in the interior, attaining voltages that could cause destructive sparking. Reports are on record of serious radium losses having resulted through neglect of this precaution.

RESULTS OF HIGHER FRACTIONATION.

The following data from a series of higher fractionations will serve to illustrate the procedure:

Results of recrystallization of radium-barium bromide.

BEFORE RECRYSTALLIZATION.

Tube No.	Weight of salt.	Ra.	$RaBr_2 2H_2O$.
	Grams.	*Milligrams.*	*Per cent.*
31	1.1705	19.9	3.16
32	1.0873	15.5	2.65
33	1.5074	43.0	5.30
34	1.4178	31.6	4.15
35	1.6325	45.0	5.13
[a] 35	1.6355	21.6	2.46
36	1.9548	23.3	2.21
37	1.4545	21.8	2.90
	11.8603	221.7	[b] 3.48

AFTER RECRYSTALLIZATION.

C–1	0.1630	76.7	87.8
C–2	1.0983	107.3	18.2
C–3	.8732	31.7	6.7
C–4	.7101	4.17	1.1
C–5	1.0265	.62	.11
C–6	1.7256	1.56	.16
C–7	3.5449	.43	.02
C–8	2.0398	.12	.01
C–9	.4542	.07	....
	11.6356	222.67	....

[a] Special.

[b] Average.

As will be noted, the total weight of salt at the start was 11.86 grams, and after recrystallization 11.64 grams. The difference was due to material adhering to crystallizing dishes in the poorer fractions. The total Ra at the start was 221.7 milligrams, and after recrystallization 222.67 milligrams. The difference was due to a difference in measurements.

Tubes C–1, C–2, and C–3 were the fractions preserved, the others were returned into the crystallizing system at suitable points.

COMMENTS ON RESULTS.

In beginning this series, tubes 33, 34, and 35 were combined and recrystallized in twelve "head" fractions directly to tube C–1. To the first mother liquor from tubes 33, 34, and 35 were added the contents of the other tubes, Nos. 31, 32, 36, and 37. This series was carried in about 15 recrystallizations up to tube C–2. The other lower fractions in the C series were obtained by further fractionation and combination of the mother liquors, as suggested by the factor 2.0.

In general, the fractionation of radium bromide from barium bromide by means of crystallization is simple and sure. No especial skill of the operator is required, as many authors lead one to believe, nor does it seem possible that the substitution of other processes, such as the adsorption of radium by means of colloidal gels or the fractionation of radium in concentrated alkaline solution would prove advantageous. The applicability of such methods should be regarded as doubtful until demonstrated on an actual working scale. There is a wide difference between commercial operation and the extraction of a small quantity of radium in the laboratory.

The time of only one man continuously is required to carry on the laboratory refining through the system indicated in figure 5, and the time of one additional man is required for four to six days each time the higher fractionation is performed.

ADSORPTION OF RADIUM.

Contrary to rather widely entertained views, the production of a precipitate, or the presence of one, in a radium-barium solution does not necessarily involve the adsorption of considerable quantities of radium from solution. As has already been pointed out, the precipitation of 700 grams of lead sulphide in ammoniacal solution carried with it only 3 out of 1,500 milligrams of radium. The recent principle of adsorption established by the work of Paneth [a] points out that any serious removal of radium should be expected only in case the radium forms an insoluble salt with the negative radical of the adsorbent. Without entering at present into discussion as to whether this removal is really due to adsorption or to ordinary chemical precipitation, it is interesting to note that the failure of radium to be removed as sulphide, together with lead, accords well with its chemical nature, as one would expect radium sulphide to be soluble. On the other hand, the completeness of its removal as carbonate, which is to be expected, has been shown by the fact that only 6.4 out of 1,500 milligrams of radium element passed into 300 liters of filtrate.

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[a] Physik. Ztschr., vol. 15, 1914, pp. 924–929; Ztschr. physik. Chem., vol. 89, 1915, pp. 513–528.

Even if barium sulphate is present in or is precipitated in a solution containing radium, the removal of the radium is small provided a large excess of barium is present. A discussion of the "protective" action of barium appears in the section on measurements (p. 92).

ACCUMULATION OF RADIUM IN LABORATORY CRYSTALLIZING SYSTEM.

It is desirable to allow several hundred milligrams of radium to accumulate in the crystallizing system. This accumulation tends to increase gradually unless special preventive means are taken, such as crystallizing out special fractions without corresponding introduction of fresh material. The following table serves to show the results of operating the system during a period of about one month:

Third balance sheet for radium in laboratory-crystallizing system.

Tube No.	Date.	Weight of radium introduced.	Total weight of salt withdrawn.	Weight of radium withdrawn.	Balance of radium in system.
	1915.	*Milligrams.*	*Grams.*	*Milligrams.*	*Milligrams.*
Balance after delivery of radium on Apr. 1..........					271.8
38..	Mar. 12.. Mar. 16..	15.3 16.7	1.463	26.7	277.1
39..	Mar. 13.. Mar. 15..	11.2 25.9	2.103	41.5	272.7
40..	Mar. 17.. Mar. 18..	22.8 19.4	2.751	25.2	289.7
41..	Mar. 20.. Mar. 22..	18.5 16.8	.9915	20.4	304.6
42..	Mar. 23.. Mar. 24..	14.3 17.6	1.551	17.7	318.8
43..	Mar. 25.. Mar. 26..	16.5 19.5	1.100	19.8	335.0
44..	Mar. 27.. Mar. 29..	20.0 9.9	1.094	22.4	342.5
45..	Apr. 1... Apr. 2...	12.1 15.3	1.759	30.8	339.1
46..	Apr. 3... Apr. 5...	12.7 10.5	1.631	41.7	320.6
47..	Apr. 6... Apr. 7...	8.5 11.1	.938	23.8	316.4
48..	Apr. 8... Apr. 9...	11.5 8.6	1.467	33.0	303.5

Changes in the richness of the deliveries into the system affect concentration in the higher fractions with a certain lag. The distribution of radium in the different vessels of the system is somewhat accidental, dependent on the size of fractions taken, acidity, and other conditions that may vary from time to time, but in general, radium tends to accumulate in the −1, 0, and +1 fractions both in the chloride and bromide systems. The total accumulation in the bromide is greater than in the chloride system on account of its greater number of fractions, the higher solubility of barium bromide, and the higher degree of concentration of the radium.

All the refining operations described in this section are carried out in a room 12 by 20 feet. The vessels of the chloride system are handled over a large, shallow copper trough to prevent possible loss of solution by "crawling," possible breaks, or other accidents. Incidentally, it may be mentioned that the refining work up to the present has been notably free from misfortunes, and that no serious losses of radium have ever occurred. Although a hood is not necessary, it would sometimes prove advantageous in carrying off acid fumes. Usually, however, solutions are not sufficiently concentrated for the acid fumes to become very objectionable.

CHAPTER V. RADIUM MEASUREMENTS.

One of the most essential factors in the successful production and concentration of radium consists in following the material being concentrated, by means of careful quantitative determinations, through all the various operations from the original ore to the final product. This involves the radioactive analysis of a large number of products differing widely in chemical and physical properties and also varying in radium content through more than a billion fold.

As is well known, elements possessing radioactivity can be detected and even quantitatively measured in quantities far below the limits of any methods based on other properties. This fortunate property more than any other makes possible the concentration of an element from an ore containing about 1 part in 200 millions, by weight, to a product of any desired purity, up to 100 per cent, with a total loss not exceeding 15 per cent.

In the course of the work described in this bulletin, the principles of existing methods of radioactive measurement have been employed, but both instruments and methods have been modified to meet the practical requirements of plant control. One of the first principles recognized is that there is no universal method of radium determination at present and that each product requires study and individual treatment suited to its own peculiar chemical and physical characteristics. Nevertheless effort has been made as far as possible to unify and standardize the methods employed. Simplicity of procedure as far as consistent with accuracy has been the object sought, and the methods herein described are the result of large numbers of determinations made during more than a year of plant operation.

Three general methods of radium measurement have been employed: An alpha-ray method suitable for solids of low radium content, where no great degree of accuracy is desired; a gamma-ray method suitable for solids with a comparatively high radium content, where accuracy is desired; and an emanation method, suitable to any substance from which the radium emanation can be quantitatively liberated, and in the use of which an accuracy of 1 to 2 per cent is obtainable.

APPROXIMATE METHOD FOR SOLIDS.

A simple method of obtaining an approximate idea of the radium content of a solid susbtance not too high in activity consists in comparing its surface radiation with that of a standard substance.[a]

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[a] See Moore, R. B., and Kithil, K. L., A preliminary report on uranium, radium, and vanadium: Bull. 70 Bureau of Mines, 1914, pp. 64–65.

The activity thus measured is essentially that of the alpha or nonpenetrating rays. Although the result obtained may be accurate so far as the surface radiation is concerned, there is evidently no certainty that this indication closely approximates the radium content of the solid. For some ores, especially those ores of closely similar origin and general character, the comparison furnishes satisfactory results, but with other ores the deviation becomes great, on account of the differences in the nature of the gangue material, the radium distribution, the "emanating power," and other variable factors.

Consequently it is evident that the method, although possessing the advantage of simplicity, has no great degree of accuracy.

Actually it has been used in the present work in two instances only—for control of the ore sorting at the mines and for the examination of the residue after nitric-acid extraction of the ore in the plant. As mentioned subsequently, the tailings, on account of their low radium and high silica content, present great difficulty of treatment by the emanation method. For this reason, and also because the low percentage of radium in the tailings allows a considerable relative deviation without invalidating the absolute results, it has been found in most cases convenient to use the solid method in testing the tailings for radium. The determinations have, however, been checked occasionally against those obtained by the emanation method.

The procedure consists simply in comparing the activity of the tailings, after they have been allowed to dry for a few days, with the activity of the original ore, both tailings and ore being spread over the same area on a plate introduced directly into the soild electroscope.[a]

GAMMA-RAY MEASUREMENT OF RADIUM.

The most accurate method for the determination of radium in salts containing an absolute quantity of not less than 0.1 milligram of radium, and having a concentration of at least 0.05 per cent is the gamma-ray method. This method involves comparing the rate of electroscopic discharge produced by the gamma radiation from a standard salt containing a known amount of radium with the gamma radiation of an unknown salt, the conditions of measurement being, of course, identical.

A standard tube should have its radium content determined by a careful comparison with the international standard or one of the subsidiary standards. The Federal Bureau of Standards possesses a standard tube containing 20.28 milligrams of radium chloride, or 15.44 milligrams of radium element, by comparison with which the standard tube of the National Radium Institute measured 10.56 milligrams of radium element.

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[a] See Moore, R. B., and Kithil, K. L., loc. cit.

If the thickness of glass of the containing tube differs from that of the standard, a correction of about 1 per cent per 1 millimeter difference of thickness should be applied. In accurate work a correction for the length of tube should also be made, which will vary with the distance from the electroscope. This correction may be determined in various ways. It has been found convenient for the purposes of the Denver laboratory to approximate the correction by shifting the standard from its normal position until one end coincides with the position that the end of the unknown would take. The percentage decrease in activity owing to slightly increased distance of the ends from the instrument thus determined, may be applied as a positive correction. Or, if preferred, the correction may be determined once for all for tubes of various lengths containing the same quantity of radium at several distances from the instrument.

The precautions to be used in sealing the salts in glass tubes have already been described (pp. 82–83). Only after a given tube has been sealed for one month or more is its gamma radiation proportional to its radium content. In making measurements of tubes sealed for a shorter time, account must be taken of the percentage rate of accumulation of emanation (and consequently the gamma radiation) according to the expression $I_t = 1 - e^{-\lambda t}$, in which I_t is the percentage accumulated at any time, t, e is the base of the Naperian logarithms, λ is the decay constant of radium emanation = 0.0075 (hour)$^{-1}$. The function $e^{-\lambda t}$ for various time intervals is solved in the Kolowrat Table A.[a]

If the gamma-ray measurement must be made within a few days after the tube has been sealed, the importance of a sharply defined starting point for the accumulation can be appreciated (see p. 82). If the assumed starting point is correct, two separate measurements at different time intervals will be in accord; if not, a new theoretical starting point must be determined as follows: The percentage increase in activity between the first and second measurements is determined. Clearly there is only one period during which this increase can take place in the given interval of time, which can be found by consulting the Kolowrat table. This figure establishes the the corrected zero point, from which the two time intervals are reckoned anew and applied to the radium measurement. A third measurement at yet another interval will serve to test the correctness of the new zero.

Measurements made in this way, after only two days of accumulation, have agreed within 1 per cent with the measurements made by the Bureau of Standards after a much longer lapse of time. The final accuracy of the gamma-ray method is considered to be 0.3 per cent.

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[a] Kolowrat, Léon, Le Radium, vol. 6, 1910, pp. 195–196; also Curie, Mme., Traité de Radioactivité vol. 2, pp. 361–362; and Chemiker Kalender, 1914, vol. 2, pp. 361–362.

Almost any form of electroscope can be employed for the gamma-ray measurement by placing between the electroscope and the source of radiation a lead screen one-eighth to one-fourth inch thick. The screen should preferably be nearer to the electroscope than to the radium tube. The interchangeable electroscope (see p. 99) with an ordinary emanation chamber has been used satisfactorily.

However, for the sake of convenience, a special gamma-ray instrument has been designed by the authors for these measurements (see Pl. XIV, *A*). It consists of a cylindrical discharge chamber, also containing the leaf system, mounted on a wooden base about 3½ feet long. The telescope is fixed directly into the ionization chamber, which is provided with a small window in the opposite side for the transmission of light. The cylinder is of brass with an interior lead lining one-eighth of an inch thick, besides which an additional lead plate (one-fourth of an inch thick) is provided outside the chamber, which may be removed if desired. The holder for the radium tube is mounted on a track running the full length of the 3-foot graduated extension, and along which it may be fixed at any point by means of a set screw. The tube holder itself is a grooved metal rod, in which the tube is held in a horizontal position opposite the middle of the discharge chamber by a single narrow spring clamp. The groove is graduated from its center in both directions to facilitate centering the tube and making length corrections.

The electroscopic procedure, with respect to charging before use, and determination of the natural leak, is identical with that described in detail for the emanation method (see p. 103).

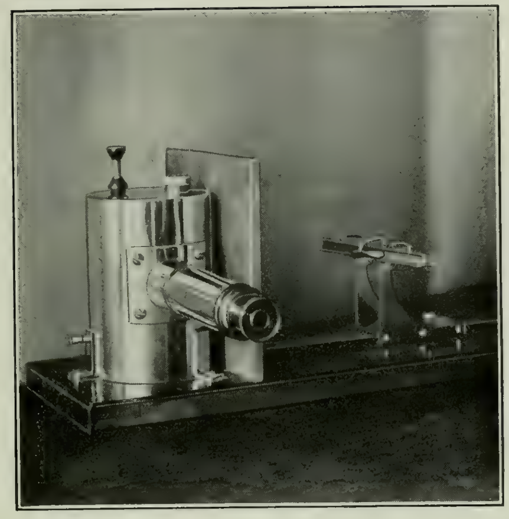
In general, the gamma-ray method is simple and satisfactory. Its accuracy may be judged from the data contained in the table on page 83, in which all the radium data reported were obtained through its use. As carnotite is free from thorium, no complications arise from the presence of mesothorium in the radium salts.

RADIUM DETERMINATION BY EMANATION METHOD.

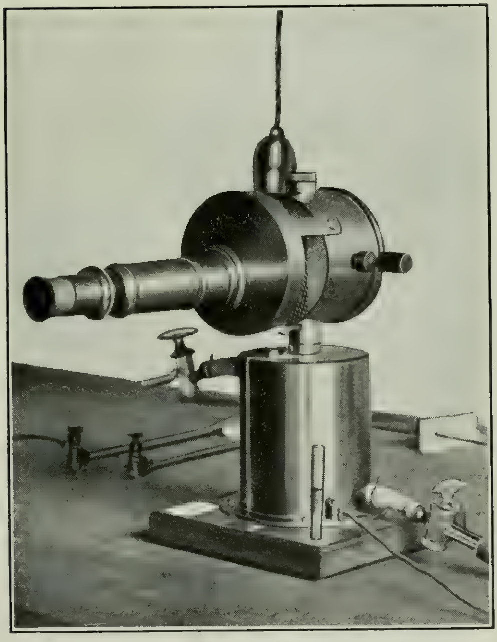
The determination of radium by the emanation method involves separating radium emanation (as a gas) from its parent radium, and measuring its quantity in a gas-tight electroscope previously standardized with a known amount of radium emanation. Analyzed pitchblende has been employed to furnish known quantities of emanation for purposes of standardization.

Three general methods of procedure may be used as follows:

(1) Release and measure the emanation from a substance in which it is in equilibrium with the radium content. This condition will



A. ELECTROSCOPE FOR MAKING GAMMA-RAY MEASUREMENTS.



B. ELECTROSCOPE WITH INTERCHANGEABLE IONIZATION CHAMBER. THE ELECTRIC LIGHT SOCKET AND WIRE ABOVE THE INSTRUMENT ARE NOT PART OF IT.

usually not be fulfilled unless the substance has been retained for a month or more in a closed container. In exceptional instances, however, the radium might be contained in a solid of such compact structure, or with a glazed surface, so that no spontaneous loss of emanation could take place. But even with a dense mineral like pitchblende, the leak of emanation, called "emanating power," amounts at ordinary temperature to several per cent. This circumstance suggests the second procedure.

(2) Liberate and measure the emanation retained in the solid and apply as correction the "emanating power," which must be determined separately and preferably after the solid has been in a closed retainer for one month.

Both of the above procedures, applicable in general to solids only, involve in practice long delays, and, although they are adapted to scientific investigation, they are not suited to radium measurement for purposes of plant control when quick results are desired.[a] The following procedure is shorter and probably preferable when its use is possible.

(3) Remove the emanation completely from a sample of the substance to be analyzed for radium, close it at once in a gas-tight vessel, and allow the emanation to accumulate for a convenient period (one to ten days). Then remove it and measure it, making a time correction to find the maximum amount that would have been formed on the attainment of equilibrium.

For removal of emanation the radium must be contained either in solution or in a state of fusion.

Some substances, like carnotite, can be deëmanated merely by heating to a high temperature, but carnotite can not be deëmanated a second time in this way, as the first heating changes its physical state so that a second heating does not produce complete deëmanation; hence heating can be used only in the month-accumulation method.

The removal of emanation from a solution may be accomplished by aspiration or preferably by boiling. Only the latter has been used by the authors and is described subsequently. Removal from a fusion may be accomplished by passing air or some other gas over the fusion, but it is preferable to bubble air through the fused mass or to produce in it an evolution of gas to insure the complete removal of radium emanation.

PROCEDURE WHEN RADIUM IS IN SOLUTION OR IN A SOLUBLE FORM.

The determination of radium in a solution can generally be conveniently carried out directly if a few precautions are carefully observed. It has been repeatedly noted that radium solutions show some tendency to lose radium from a solution on standing, a phenomenon that manifests itself in a decrease of the successive quantities of emanation that can be obtained from the solution. This tendency of radium solutions has resulted in the almost complete abandonment of the practice of preserving the solutions over long periods of time for standardization purposes, a practice that produced serious errors in some earlier work. The loss is to be attributed to precipitation or adsorption in a form that will not readily give up its emanation. In general, the presence of precipitates or suspensions in the solution should be avoided, though this source of error has frequently been exaggerated.

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[a] For further details of the practice in the use of methods 1 and 2, see Lind, S. C., and Whittemore, C. F., The radium-uranium ratio in carnotites: Tech. Paper 88, Bureau of Mines, 1915, pp. 10–20.

Loss of radium by precipitation through small amounts of sulphate, originating either in the glass walls of the containers or in the reagents, should be guarded against. For analytical purposes a suitable preventive measure is adding a large excess of "protective barium." On account of the chemical similarity of barium and radium any precipitant that affects the radium will be removed by the large excess of barium, or, rather, radium and barium will be precipitated in the same proportion in which they occur in solution, and therefore only a minimal quantity of radium is removed. Furthermore, it is desirable that the solution contain nitric acid up to the solubility limit of barium nitrate, which is rather low in the presence of nitric acid of 50 per cent strength. The object of the nitric acid is to prevent the removal of radium as basic salt, which may be formed in neutral chloride or bromide solutions by the action of the alpha particles; hot concentrated nitric acid also has the well-known property of rendering barium (radium) sulphate more soluble (see p. 28).

The two essentials in handling radium solutions for analytical purposes consist, then, in maintaining an excess of barium and a fairly high concentration of nitric acid. Following are described treatments for three kinds of solutions, under one of which any given solution will be included. The reasons for the prescribed treatment will be clear from the foregoing discussion.

TREATMENT FOR SOLUTION CONTAINING BARIUM IN LARGE EXCESS OVER RADIUM.

For a solution containing barium in large excess over radium the treatment is as follows:

Place a suitable portion of the solution—such as will contain about 1×10^{-8} gram of radium—in a small Jena flask, and add to it a suitable quantity of 1:1 nitric acid. Add a few glass beads, and boil 5 to 10 minutes to remove all emanation. Allow slight cooling and then close the flask tightly with a one-hole rubber stopper provided with a glass tube drawn out above to a capillary tip. Seal the tip while some steam is still in the flask, in order to provide a partial vacuum, which should be maintained until the flask is again opened, thus affording a proof that no outward leak of gas has taken place. Note the exact time and date of sealing.

TREATMENT FOR SOLUTIONS CONTAINING LITTLE OR NO BARIUM.

The treatment for a solution containing little or no barium is to add a suitable portion to 1:1 nitric acid which is saturated with barium nitrate, and to proceed as in the treatment described above.

TREATMENT FOR SOLUTION CONTAINING NO BARIUM BUT AN EXCESS OF A BARIUM PRECIPITANT.

A solution that contains no barium but an excess of barium precipitant, such as sulphate or carbonate is usually a filtrate from a radium-barium precipitation, and requires especially careful treatment; otherwise highly erroneous results will be obtained. If such a solution were boiled off and sealed directly, the results would usually be low, as much as tenfold, and the solution would continue to decrease in emanating power the longer it remained standing. This behavior has led the authors to the belief that in the precipitation of radium in low concentration, or at any rate, its removal, whatever the process, is a progressive time reaction. On the other hand, unduly high results may be obtained, especially in using the correct procedure, if the sampling has been incorrect, for example, when too much of the fine (frequently invisible) precipitate relatively rich in radium has been obtained in a given fraction of the liquor.

Such a relatively rich fraction might easily be obtained in siphoning the liquid from above a sulphate precipitate, if the sample of liduid were taken near the end of the process. It has been found necessary to take samples at intervals during the entire siphoning process and to make a composite solution.

PROCEDURE FOR LIQUIDS CONTAINING EXCESS OF SULPHATE OR CARBONATE.

The detailed procedure for treating a liquid containing an excess of sulphate or carbonate, but no barium, is as follows: An excess of barium salt is added to the liquid, and the precipitate is filtered off. The filtrate containing an excess of barium is made acid with nitric acid to the point of precipitation, and is given the treatment outlined for a solution containing barium in large excess over radium. The precipitate, if barium sulphate, is fused with four to five times its weight of a fusion mixture (1:1 Na_2CO_3 and K_2CO_3), and is treated as described later for fusions. If the precipitate is barium carbonate, it is dissolved in nitric acid containing sufficient sulphuric acid to precipitate an amount of barium sulphate convenient for fusion, which is filtered off. The filtrate that is obtained may be combined with the original filtrate, and given the treatment as described for a solution containing barium in large excess over radium. All radium is then contained either in the filtrate with excess of barium or in the fused precipitate. Both of these fractions are closed simultaneously (within 15 minutes), so that the time of accumulation will be the same for both lots of emanation, which can be later introduced into one electroscope to determine the total radium.

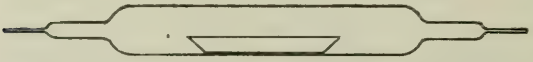

FIGURE 6.—Laboratory apparatus for fusing radium-barium sulphate.

FUSION METHOD FOR RADIUM DETERMINATION.

If the radium is contained in a substance not readily soluble, such as a radium-barium sulphate, fuse a suitable quantity in a small platinum or porcelain boat with four to five times the weight of sodium or potassium carbonate, and note the exact time of cooling. Close this boat in a glass tube as shown in figure 6. Allow the emanation to accumulate two or more days. Connect the glass tube at one end to a highly exhausted electroscope and at the other end to a stopcock. Break the glass tips inside the rubber connection, and exhaust the air from the glass tube into the electroscope several times, leaving enough vacuum in the electroscope chamber to accommodate the gas to be introduced later. Break the glass tube, remove the boat and its contents, wrap in a filter paper, and place in the neck of a flask as shown in figure 7; it is then ready for treatment with 1:1 nitric acid after the flask has been connected with the gas burette, as shown in figure 8. In this treatment the flask is tipped until the acid comes in contact with the carbonate fusion, thus beginning a gas evolution. The stopcock is immediately opened to the gas burette above and the boat and contents are then thoroughly wet with acid and jarred down from the neck of the flask into the body of the acid. As regards larger fusions, the evolution of carbon dioxide may become rapid and care should be taken in handling them, but in small fusions not exceeding 1 gram the boat may be shaken directly down into the acid, which should be heated

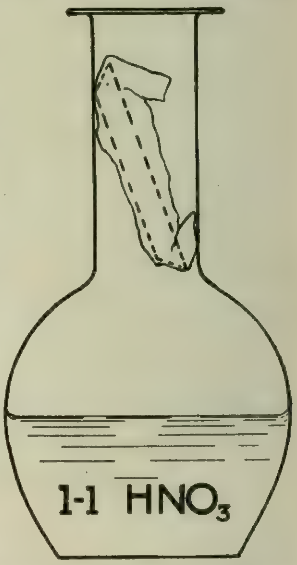

FIGURE 7.—Carbonate fusion in flask for nitric acid treatment.

to boiling as soon as the gas evolution begins to slacken. All of the carbon dioxide is, of course, absorbed by the sodium hydroxide solution in the gas burette. The boiling off from this point on is performed as with solutions discussed below.

For small fusions of substances running about 1 part of radium per million, such as crude radium-barium sulphate and high-grade pitchblende, of which a sample of 20 to 40 milligrams would be taken, the authors have employed small handmade boats, each one being folded from a strip of platinum foil $\frac{1}{1000}$ inch thick, ¾ inch broad, and 1½ inches long, the finished boat being about 1 inch long and about ¼ inch in cross section. Such boats have been found convenient, can be made at small expense, and have a reasonably long life if the material to be fused does not contain lead. For substances poorer in radium, necessitating larger samples, the authors have employed porcelain boats, flasks holding as much as a liter having been used for the solution in some instances. The gas evolution is so vigorous that a gas burette with an enlarged bulb at the top should be used to furnish an increased amount of sodium hydroxide solution.

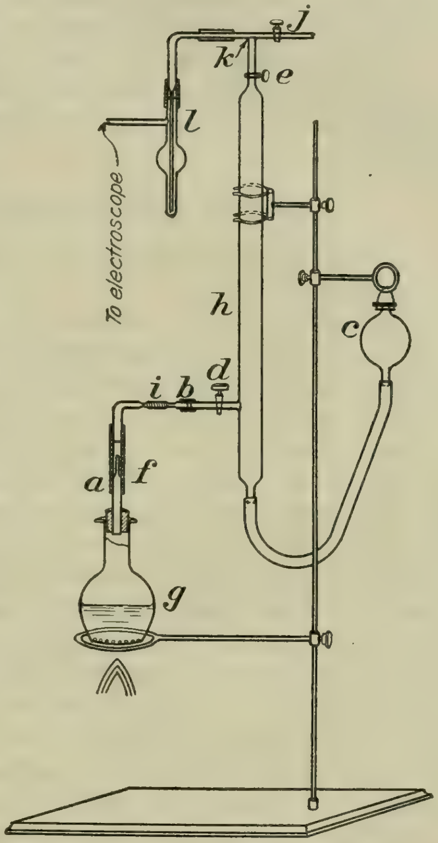

FIGURE 8.—Apparatus for boiling off, collecting, and transferring emanation into electroscope.

DIRECT FUSION METHOD.

If desired, one can use a fusion both before and after the accumulation of emanation instead of dissolving the fusion in acid. If this is done, as soon as the initial fusion cools, the thin platinum boat is unfolded, and the fusion is put into a Jena glass tube of the form shown in figure 6, and held in place at both ends by small glass-wool plugs, which react with the carbonate in the second fusion, giving an evolution of carbon dioxide, which assists in removing the emanation. Usually in this method the gas is not passed into a gas burette at all, but the exhausted electroscope is attached and allowed to pull a current of air directly through the hard-glass tube while it is being strongly heated with a Meker burner until the vacuum is exhausted. However, this practice would not be allowable except with substances free from thorium.

The tube is heated until it collapses completely, but collapse should not occur until a large volume of air has passed over the fusion. A small drying bulb is placed in front of and another is placed behind the tube. Between the hard-glass tube and the drying bulb next to the electroscope a small tube containing potash solution is introduced to prevent carbon dioxide from passing into the electroscope.

No gas except air should ever be introduced into the electroscope with the emanation because the specific ionization of different gases differs from that of air, and the difference may cause a large error in the comparison.

BOILING OFF EMANATION FROM SOLUTIONS.

For boiling off emanation from solutions, the procedure prescribed is as follows:

Set up apparatus as shown in figure 8, wiring the rubber connections at *a* and *b* to insure tightness. Put into the leveling bulb *c* a stick of sodium hydroxide 2 to 3 inches long, or more if a large quantity of carbon dioxide is to be absorbed; make sure that stopcock *d* is closed and stopcock *e* open; pour boiling distilled water into the leveling bulb and allow the alkali to go into solution. If the boiling is too violent, put a one-hole stopper lightly into the mouth of the leveling bulb. After the alkali has gone into solution raise the leveling bulb until the gas burette is filled to the stopcock *e*. If the quantity of air to be boiled off is small, some air may at first be left in the gas burette. Close stopcock *e* and lower bulb *c* to its original position. Break the glass tip *f* inside the rubber tubing at *a*, and slowly open *d* to ascertain whether there is vacuum in the flask *g*. If so, close *d* again and begin to heat flask *g* over wire gauze. Test the vacuum every few seconds and as soon as the pressure is outward open *d*, and cause the flask to boil vigorously. Continue boiling until live steam has heated to boiling all the liquid in the gas burette *h*. This boiling should never be less than 5 minutes, and sometimes 10 to 15 minutes' boiling is desirable.

After the glass tip *f* has been broken the liquid is likely to be carried upward by steam and in some instances has lodged in the stopcock *d* and caused serious explosions. As a precaution, a roll of thin platinum foil can be introduced into the glass tubing, as indicated at *i*, or the stopcock *d* may have a wide bore, which also obviates the danger mentioned.

After the boiling off has been completed, remove the flame, and as soon as the liquid begins to draw back through the stopcock *d* close the stopcock and remove the flask entirely. Evacuate the electroscope chamber to a suitable vacuum, either by means of an aspirator or, more conveniently, a hand pump; connect the sulphuric-acid microdrying bulb *l* to the electroscope and to the gas burette, as indicated in figure 8. Be sure that stopcock *j* is closed; open first the cock of the electroscope for a moment and reclose it; then slowly open stopcock *e* to full width, and then gradually open the stopcock to the electroscope, allowing the gas to bubble through the microdrying bulb at a fairly rapid rate. When the liquid in the gas burette has risen exactly to the point *k*, close stopcock *e* and open stopcock *j*, allowing dry, dust-free air, which should preferably be taken from outside the laboratory, to sweep out the connections for a few minutes; then close the stopcock to the electroscope, reopen stopcock *e*, and allow the liquid in the gas burette to fall back 3 or 4 inches below the shoulder; close *e*, and then pour off all excess liquid out of *c;* close *j* and again open *e* to the electroscope, allowing air to bubble from the bottom of the gas burette *h* through its entire length to insure the removal of any emanation that may have remained dissolved in the liquid. This precaution is perhaps unnecessary, as the hot sodium hydroxide solution certainly does not take up much emanation, but nevertheless the precaution is in the direction of accuracy. Air should be allowed to bubble into the electroscope chamber until normal pressure has been almost restored.

The procedure just described for boiling off radium emanation is used for carbonate fusions introduced into acid, and also in handling any solids that are to be dissolved directly. For example, ground pitchblende and carnotite ore, which may be wrapped in filter paper in the way in which a fusion is wrapped (fig. 7) or sealed in small glass bulbs, which are opened by being crushed against the bottom of the flask by tapping on the glass stem projecting through a second hole in the rubber stopper.[a] To economize time, two of the boiling operations may be carried out simultaneously by the same operator.

METHODS OF RADIUM DETERMINATION APPLICABLE TO VARIOUS SUBSTANCES.

The methods best adapted to determination of the radium in the various products that would usually present themselves for radium analysis in plant control are indicated below.

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[a] See Lind, S. C., and Whittemore, C. F., The radium-uranium ratio in carnotites: Tech. Paper 88, Bureau of Mines, 1915, p. 13.

PITCHBLENDE.

High-grade pitchblende is low in silica and readily soluble in hot 1:1 nitric acid. Hence, solution as well as fusion methods are applicable. As the radium-uranium ratio is normal, the radium content may also be calculated from a uranium analysis.

CARNOTITE.

Carnotite is readily soluble in hot 1:1 nitric acid and one of the best methods for its radioactive analysis is solution from a sealed glass tube in which it has been inclosed for a month. Strong ignition (as with Meker burner) of the ore also removes the emanation initially, but second ignition does not do so; therefore, the ignition method is limited to carnotite that has been in a closed container for a month or more. The high silica content of carnotites imparts viscosity to the carbonate fusion, which renders removal of emanation by diffusion difficult. Higher temperature [a] or direct bubbling of air through the fusion doubtless tends to obviate the difficulty, but the authors' experience in general has not been favorable to the use of the fusion method for carnotite. The radium-uranium ratio is normal for large lots of well-sampled ore, and the radium may, hence, be calculated from the uranium content.

CARNOTITE RESIDUES AND TAILINGS.

All the difficulties arising in the analytical treatment of carnotite are manyfold multiplied in the treatment of extracted tailings, with the additional difficulty that as the radium content has already escaped solution, solution methods are not logically applicable. As already stated, the approximate alpha-ray method for solids gives results sufficiently accurate for most purposes (see p. —). In order to apply the emanation method it is necessary, first, to remove the silica from at least a 10-gram sample with hydrofluoric acid before proceeding with the fusion method.

Neither with carnotite nor tailings is it practicable to dissolve the carbonate fusion in acid, as the high silica content soon forms an impervious gel around the surface which prevents further attack.

NITRIC ACID FILTRATE FROM CARNOTITE ORE.

Nitric acid filtrate from carnotite ore may be boiled and sealed directly with or without the addition of barium nitrate, as the original ore contains a large barium excess relative to the radium.

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[a] See Schlundt, H., Trans. Am. Electrochem. Soc., vol. 26, 1914, p. 170.

BARIUM (RADIUM) SULPHATES OR SULPHIDES.

Barium (radium) sulphates or sulphides are fused with carbonate mixture in platinum or porcelain boats, described on page 95, sealed in glass tubes for accumulation, and either dropped into acid or fused directly.

SULPHATE OR CARBONATE FILTRATE.

Sulphate or carbonate filtrate must be handled with all the precautions prescribed for liquids of this character on page 93.

BARIUM (RADIUM) CHLORIDE OR BROMIDE LIQUORS OR CRYSTALS.

Barium (radium) chloride or bromide liquors or crystals may be treated according to the treatment prescribed for a solution containing barium in large excess over radium (p. 92), after suitable dilution for richer fractions from the crystallizing system. The dilution necessary becomes considerable, as much as one to a million in some instances. This dilution is carried out with pipettes and measuring flasks according to the usual methods of volumetric analysis, but involves unusual care in rinsing the vessels used for such large dilution.

The principles already described should suggest a suitable mode of procedure for any other substances that may present themselves for radioactive analysis in connection with the production of radium. But in dealing with any new substance, one should always try several methods for control before final selection.

CONSTRUCTION AND USE OF INTERCHANGEABLE ELECTROSCOPE.

A modified form of the aluminum or gold-leaf electroscope of the C. T. R. Wilson type (Pl. XIV, *B*) has been found entirely satisfactory for all quantitative purposes. The chief modification consisted in making the upper part of the instrument carrying the telescope and leaf system separable from and interchangeable with a large number of gas-tight ionization chambers. This arrangement enables one to carry out a number of emanation determinations in a day without material additional expense, as the emanation chambers can be easily reproduced. The usual type of Wilson electroscope was further modified by building the telescope into an extension front from the leaf chamber, so that the relative positions of electroscope and leaf remain absolutely fixed. Too much stress can not be laid on the importance of this feature. During the year in which an instrument of this type has been in daily use the leaf has not been disturbed, nor has refocusing been necessary; an advantage of the utmost importance in maintaining the calibration constant. Effort has been made to design a simple instrument that could be constructed, with the exception of the telescope, by any mechanic.

DETAILS OF CONSTRUCTION.

A description of the parts of the electroscope (Pl. XIV, *B*, and fig. 9) and of the emanation chamber follows. The emanation chamber is a gas-tight brass cylinder 4 inches high and 3½ inches in diameter with a volume of about ½ liter. The brass wall of the cylinder is about $\frac{1}{16}$ inch thick, except the bottom plate, which is about ⅛ inch thick. The bottom plate projects ½ inch outside the cylinder and is screwed to a wooden base 6 by 6 inches. This projection also carries a binding post for grounding the instrument. The vertical cylinder projects into the base, into which it is carefully soldered so as to make a gas-tight joint.

On account of the difficulty of obtaining gas-tight brass stopcocks, glass ones have been used and are connected to the plain brass outlet tubes *o* (fig. 9) from the cylinder by means of heavy rubber tubing wired on and with the ends covered with piscein glue. These outlet tubes are ¼ inch in internal diameter and placed ½ inch from the top and bottom on opposite sides of the cylinder.

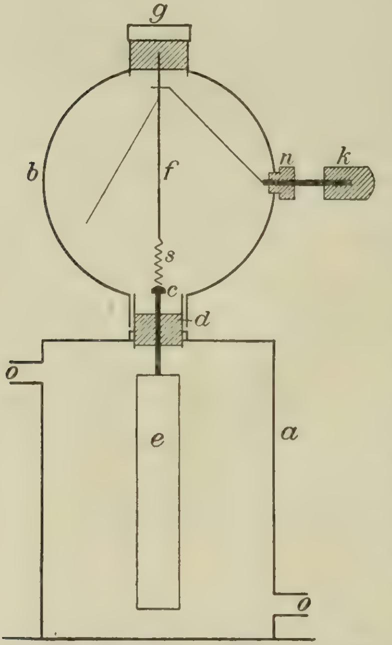

FIGURE 9.—Cross section of electroscope with detachable ionization chamber (one-third size).

The electrode *e* is a brass cylinder ½ inch in diameter, projecting downward in the vertical axis of the cylinder to within ½ inch of the bottom and clearing the top by the same distance. The electrode is suspended by a small brass rod ⅛ inch in diameter, which screws into the top of the electrode, passes upward through the insulating material, *d*, and terminates in a small conical cap, *c*, serving to make metallic contact with the leaf system above.

The leaf system *f* is supported from the top of the cylinder where it is held in place by the sealing-wax insulation set in a milled-head cap, *g*, which screws into a vertical collar on the cylinder ¼ inch in height. The cap is hollowed out inside to contain the insulating wax, from which a flat brass rod, *f*, ¼ inch broad, about $\frac{1}{16}$ inch thick, and 2¼ inches long, projects downward, terminating below in a light brass spring, *s*, to make a slight contact with the conical top of the electrode of the ionization chamber. The spring should touch the electrode lightly or it will throw the leaf system out of position.

The aluminum leaf itself, about 2 inches in length, is attached to a small offset at the top of the brass rod by a moisture contact. The whole leaf system may be removed by unscrewing the cap without disturbing the rest of the instrument. If the cap does not screw down tightly into the desired position, a drop of solder may be placed across the joint between the screw head and the collar to prevent accidental displacement of the leaf.

The charging device *k* (fig. 9) consists of a brass rod threaded horizontally through a hard-rubber insulation *n*, in the side of the case. Inside the case the rod slopes upward at an angle of 45° and then extends horizontally, so that contact can be made with the brass rod of the leaf system while being charged, or so that it may be turned and grounded against the wire grating of the outer case.

A collar ¾ inch long below the bottom of the cylinder makes a fairly snug contact fit over the collar on top of the discharge chamber and serves as support. A wooden frame is used to hold the upper half of the instrument when it is detached from the base.

One of the best insulating materials for an instrument of this type is high-grade sealing wax, such as "bankers' specie." It has the advantage over sulphur of furnishing both gas-tight connection and good electrical insulation, and is, of course, much less expensive than amber. The sealing-wax insulation is bridged across the bottom of a cylindrical neck ⅜ inch in internal diameter and 1 inch high above the top of the cylinder. It is desirable to have the minimum layer of wax that will give the necessary strength. A layer ¼ inch deep should be ample. The additional height of the neck merely furnishes a friction support for the upper part of the instrument. The electrode and insulation can be removed by unscrewing the whole collar, which is threaded into the upper brass plate of the cylinder $\frac{3}{16}$ inch thick. The collar screws down on a thin lead or rubber washer to insure gas tightness. The removal of the collar and electrode enables one to melt the wax into place with great ease and also to place the electrode in position without disturbing the soldered joint at the bottom of the emanation chamber.

A friction cap fitting snugly down over the neck and the projecting electrode stem protects the insulation from contamination when detached from the upper part of the instrument.

The leaf system and telescope are carried by the upper part of the instrument (Pl. XIV, *B*) and have the advantage over some instruments of being fixed in a perfectly rigid position with respect to each other.

The horizontal cylinder *b* (fig. 9) containing the leaf system is 1¼ inches deep and 3¼ inches in diameter; the ends are closed by sheet mica held in place by steel-wire rings which fit in grooves in the edge of the cylinder in the same way that an automobile tire is held in place. This arrangement has proved most convenient and far preferable to the use of screws. Inside the mica plates and in close contact with them, fine iron-wire gauze serves to conduct off any stray electrical charge. Circular openings in the gauze 1½ inches in diameter furnish a clear field of vision opposite the leaf system.

Opposite the aluminum leaf is a vertical brass plate (not shown in diagram) parallel to the leaf, which may be pushed in so that it almost touches the leaf, and thus protects it from mechanical disturbance during transportation. Whenever the instrument is in use this protector should be withdrawn against the outer case. It may be turned crosswise, if necessary, to remove it as far as possible from the leaf.

Instead of suppporting the telescope on an upright fixed to the same wooden base as the rest of the electroscope, it appeared preferable to fasten it firmly to the case carrying the leaf system. Three arms, such as the one shown in Plate XIV, *B*, carrying a solid brass vertical plate, are firmly screwed onto the case of the leaf system. The telescope fits tightly into a heavy horizontal collar which is screwed into the front plate which is thickened by two small plates to increase the depth of the screw thread. The telescope may be fitted firmly into place and soldered after focusing, or the collar may be split and carry a tightening screw for readjustment.

The telescope used is a Bausch & Lomb type with a 32-mm. objective and a No. 5 eyepiece, carrying a micrometer scale serving to measure the rate of discharge of the leaf. The eyepiece fits firmly into its case, so that its rotation is difficult after the micrometer scale has been set parallel to the leaf.

By means of a charging battery a charge can be maintained for some time on the instrument. Otherwise one can charge with amber or hard rubber, with an ordinary rubber comb for example.

The glass tube (see Pl. XIV, *B*) fixed in the wooden base of the instrument about 1½ inches from the cylinder serves to hold a small sealed tube of radium salt used in controlling the calibration of the instrument. A suitable quantity of radium (about 1 milligram of element, in a sealed tube) furnishes a constant source of penetrating radiation, which may be conveniently employed to control the calibration by measuring the rate of discharge when this tube is placed in the glass tube fixed into the base, and by making comparison with the discharge obtained in the same way at the time of calibration with emanation. Such a measurement can be made in a few minutes and saves a great deal of time in avoiding the repetition of the calibration with emanation, if no marked change is found to have taken place in the rate of discharge.

USE OF ELECTROSCOPE IN EMANATION METHOD.

The principle underlying the use of the emanation electroscope is that, in a given discharge chamber containing at two different times different quantities of radium emanation, the ionization and consequent rate of discharge will be proportional to the quantity of emanation present. If in one case this quantity is known, the unknown quantity can be determined by a direct comparison of the two rates of discharge. The principle seems simple and with the observation of a few essential precautions is really so in application.

Owing to the rapid decomposition of radium emanation into the series of elements, radium A, B, and C, each of which deposits as a solid "active layer" on the walls of the chamber, and contributes materially to the activity, it is necessary to wait three hours after the introduction of the emanation for the active deposit to have reached a maximum. This maximum is maintained with little change between the third and fourth hours, and hence the measurement of the rate of discharge may be made during this period.

It is also to be noted, however, that these active decomposition products of radium emanation carry a positive electrical charge when formed, and hence the position at which they are deposited in the chamber will be somewhat dependent on the electrical field to which they are exposed during deposition, and in turn the ionization and rate of discharge will be influenced. It would seem simple to allow the deposition of the active layer always to take place with no electrical field, but the difficulty here is that as soon as the field is made for measuring the rate of discharge, a shift in the position of newly formed RaA takes place so rapidly that even in the few minutes necessary for measurement, the rate of discharge may change considerably either increasing or decreasing according to whether the new position of RaA is more or less favorable to ionization. To overcome this difficulty one practice is to keep the electroscope charged during the entire three hours of activation, but this procedure may be inconvenient if different instruments are being used on the same charging line, and it has been found more satisfactory in the laboratory to charge for 15 minutes before the measurement. Thus any shift of RaA can be practically completed, and any shift of RaC (through RaB, an a-rayless product) will not have proceeded to any considerable degree.

The measurement itself consists in determining with a stop watch the time elapsing during the passage of the leaf over a certain part of the scale, reading being made always between the same scale divisions. Two or three closely agreeing measurements suffice, but if the deviations are greater than 1 per cent, an average of 10 measurements is taken. The discharge is then reckoned in terms of scale divisions per second. From the result is subtracted the "natural leak" of the instrument, which is determined before the introduction of emanation. Even with a double contact of wax insulation, the natural leak maintains a low value of about .0003 to 0.005 divisions per second.

Another source of error, which seems especially pronounced in using sealing wax as insulation, is in the so-called "electrical soak" of the insulator, meaning that a certain time is necessary for the insulator to become fully charged. Unless sufficient time is allowed (not less than 15 minutes) for this process to complete itself, the rate of discharge is erratic.

The procedure in the use of the electroscope is then as follows:

1. Set up electroscope as shown in Plate XIV, *B*, and charge for 15 minutes from a battery with just sufficient voltage to hold the leaf on the part of the scale to be used later.
2. Observe the natural leak during 15 or more minutes.
3. Carry out the calibration control by means of penetrating rays if radium is available for this purpose.
4. Detach the top and evacuate the lower chamber to the desired vacuum.
5. Pass the emanation-air mixture through a sulphuric acid drying tube into the evacuated chamber and restore normal pressure.
6. Allow the emanation to stand in the discharge chamber for three hours.
7. Charge for 15 minutes as before.
8. Take three readings if agreements are good, or ten if deviations are greater than 1 per cent.
9. Clean out the emanation chamber by drawing dry, dust-free air through it for some time (over night if convenient).
10. Calculate the discharge and subtract the natural leak, expressing both in divisions per second.
11. Compare the corrected discharge with the calibration of the instrument to determine the quantity of radium under measurement, taking time corrections into consideration.

CALIBRATION OF ELECTROSCOPE.

The calibration of the electroscope is carried out in exactly the same way as in ordinary measurement, except that a known quantity of emanation is introduced. This known quantity may be obtained in two ways, as follows:

1. From a standard solution of some radium salt by passing air through it until its emanation is all transferred into the electroscope. This practice has two disadvantages, the necessity of having and taking care of such a standard solution, and the uncertainty attaching to the quantity of radium emanation removed from it, owing to

the great tendency of radium in such small quantity to be precipitated out in part or to be occluded in the walls of the vessel during prolonged standing. In short, the practice of employing standard radium solutions, though rather general, is not to be recommended, and has been pronounced unsatisfactory at the Radium Institute [a] in Vienna.

2. The preferable practice is to use high-grade analyzed pitchblende, a suitable quantity being dissolved for each standardization, and the quantity of radium being calculated from the uranium analysis. The quantity of radium emanation obtained on dissolving the pitchblende will not correspond exactly to the radium content because a small fraction (2 to 5 per cent) of the gas diffuses from the ore; this fraction, termed the "emanating power," must be determined by sealing a quantity of the ore in a tube for a month or more, and drawing off the emanation into an electroscope by the passage of air. The emanating power thus determined in the standard sample is used as a subtractive correction. Convenient quantities of radium emanation are those that will produce a discharge of the order of 1 to 2 scale divisions per second.

EXAMPLE.

Given a standard pitchblende containing 60 per cent uranium metal and having an emanating power of 3 per cent. If the Ra/U ratio is 3.33×10^{-7}, 1 milligram of pitchblende contains 2×10^{-10}, grams of radium, but as only 97 per cent of this radium can give off emanation, 1 milligram of pitchblende on being dissolved will furnish emanation equivalent to 1.94×10^{-10} grams of radium. For the electroscope herein described use 20 to 40 milligrams of high-grade pitchblende.

Contamination of the discharge chamber may come about through the gradual accumulation of active deposit on the inner walls, which results in the increase of the natural leak of the instrument. For this reason more emanation than is necessary for a measurement is never introduced. The removal of emanation from the chamber should take place at once after the completion of the measurement, and to avoid the introduction of any emanation that may be present in the laboratory air, air is drawn from the outside, being passed through a train of cotton batting to remove dust and through sulphuric acid to remove moisture. Should the discharge chamber become contaminated in spite of all precautions, the chamber is opened and the walls thoroughly washed with dilute (1 to 3) nitric acid, followed by washing with distilled water and drying. This operation is repeated until the natural leak is sufficiently reduced. Contamination of the insulation itself usually necessitates its complete removal.

In measurements of great accuracy it is desirable to calibrate each discharge chamber separately, but by taking greater precaution in the construction and position of the electrode each chamber can be made to have the same electrical capacity and hence one calibration will serve for all. It seems practicable to reproduce chambers that shall have the same calibration value within 2 per cent.

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[a] Meyer, Stefen, ——, Sitzungsb. K. Akad. Wiss. Wien, Mathem.-naturw. Klasse, Bd. 122, June, 1913, pp. 1085–1114.

The convertible electroscope may also be used with other forms of discharge chamber than that used for emanation. For example, it may be used in water analysis by attaching it to a water chamber of the fontactometer type, or may be attached to an open α-ray chamber such as is used for the cursory examination of ores, or to any other desired form of discharge chamber.

ACCESSORIES FOR ELECTROSCOPE.

Accessories for the interchangeble electroscope are listed below.

A wrench for removing the collar carrying the insulation. This is used only in renewing or remelting the insulation. This is done only when the gas leak or the electrical leak has become unduly high. In dry climate, sealing wax dries out rather rapidly, and it is found necessary to remelt the sealing wax about once in one or two months. The operation is simple, but necessitates a new standardization of the chamber.

Two brass dies, used in remelting or replacing the insulation to hold the wax below the electrode.

One brass cap with hole, used in centering the electrode during remelting the insulation.

One hard-rubber cap with brass binding screw head, used in charging one chamber while the regular top is being used on another chamber.

CHAPTER VI. RECOVERIES, LOSSES, AND COST DATA.

RECOVERIES AND LOSSES.

RECOVERY OF URANIUM.

In the extraction process practically all of the uranium in the ore is dissolved in the nitric acid, a little remaining in the insoluble residue because of incomplete washing. An average of 2.3 per cent of the uranium oxide in the ore has remained in the residue, varying in different carload lots from a mere trace to about twice the average. A more thorough washing would remove practically all of this uranium, but would considerably increase the volume of liquid to be handled and evaporated.

As already indicated (p. 50) the loss in the iron-calcium precipitate precipitate has varied, with the amount of sodium carbonate used and the length of time of heating the solution. In the early stages of the work most of the precipitate contained 1½ to 2 per cent U_3O_8 on the dry weight, or 15 to 20 per cent of the oxide in the original ore. This loss was afterwards considerably reduced, mainly by boiling the solution for a longer time and washing the precipitate more thoroughly. The iron-calcium precipitate from some of the carload lots contained as little as 0.48 to 0.50 per cent U_3O_8, representing about 5 per cent of the oxide in the original ore. The U_3O_8 content of the iron-calcium precipitate obtained from the last six carload lots treated averaged 0.7 per cent.

The original plan (see p. 52) called for a double precipitation in order to recover this uranium and the associated radium and vanadium, but it was found that the cost exceeded the value of the products obtained. All efforts were then bent toward raising the yields without reprecipitation.

If, after the precipitation of the sodium uranate, the solution is heated for one hour, practically all of the uranium is precipitated, only a trace appearing with the iron vanadate.

The recovery of the uranium as sodium uranate has, of course, varied with the losses, the extremes being between 75 and 94 per cent. The average on the last 10-carload lots treated has been 84.4 per cent.

RECOVERY OF VANADIUM.

The process described in this bulletin could not be recommended were the recovery of the vanadium in the ore the main object. Hydrochloric acid, under plant conditions, will extract the vanadium from carnotite more efficiently than will nitric acid, because the reducing action of hydrochloric acid prevents the vanadium from separating as vanadic acid. In this respect even sulphuric acid is better. The chief recommendation for using nitric acid is, therefore, the recovery of radium rather than vanadium. Indeed, it was found in the early operations that any attempt to extract the larger part of the vanadium almost invariably resulted in the precipitation of vanadic acid, retarding filtration and reducing the recovery of radium. Carnotite itself is readily soluble in nitric acid, but the other vanadium minerals present, especially the silicates, are decomposed only after long boiling. A considerable loss of vanadium, therefore, takes place at the start, owing to the insolubility of the vanadium minerals other than carnotite. In order to prevent the separation of vanadic acid, the ore has been heated only as long as the solution remained green, heating being discontinued at once if the solution has showed any tendency to become brown. The main object, therefore, has been to recover radium even at the sacrifice of some of the vanadium. The vanadium content of the ore used has varied from 3.46 to 5.43 per cent V_2O_5, and ore carrying less than 5 per cent presents no difficulties in treatment; however, if this proportion is largely exceeded, the rapidity of filtration is affected, resulting in some loss of radium.

Under the above conditions only about 45 per cent of the vanadium in the ore goes into solution. The iron-calcium precipitate involves a further loss. If sodium carbonate is run into a carnotite acid leach, so that the liquid is acid during most of the time, the vanadium losses will be large even though the carbonate is finally added in excess. Iron vanadates are seemingly formed near the neutral point and after precipitation are redissolved only slowly by the carbonate. In a small experimental plant that used this method to separate the uranium and vanadium from the iron and calcium the iron precipitate obtained carried 15 to 20 per cent V_2O_5. However, if the acid liquor is run into a boiling solution containing an excess of sodium carbonate, as already described, the iron-calcium precipitate obtained need not average more than 2 per cent V_2O_5, and the proportion may be reduced even to 1 to 1.25 per cent under favorable conditions. As explained on page 55, the ruling factor is the length of time the solution is boiled and how much excess carbonate is used. Of course, a point is finally reached where the additional recovery does not pay for the increased expense.

The sodium uranate has carried on an average 8.1 per cent V_2O_5, the limits being 5.2 to 9.4 per cent. If the salt fusion method is used to refine the sodium uranate, practically all of this vanadium is recovered, as the refined sodium uranate on an average carries less than 0.2 per cent V_2O_5. The iron vanadate obtained in the recovery of this vanadium is of exceedingly high grade, most of it containing about 45 per cent V_2O_5. Seemingly, in the melt the vanadium is completely oxidized to meta-vanadate.

The sodium nitrate filtrate from the iron vanadate may or may not contain vanadium, depending on the method of precipitation. If the precipitation is properly done, the sodium nitrate will carry only a mere trace of vanadium, hardly enough to give a qualitative test.

Lately, on an average 55.5 per cent of the vanadium in the ore remains in the residue, and 13.6 per cent remains in the iron-calcium precipitate, while 8.1 per cent appears in the sodium uranate and 21.4 per cent in the iron vanadate. The total average recovery in vanadium, including that from the sodium uranate is therefore a little less than 30 per cent.

RECOVERY OF RADIUM.

When an element exists in an ore in the proportion of 1 part to 200,000,000, its extraction and recovery present difficulties not ordinarily encountered in metallurgy. A recovery of 60 to 70 per cent or even 50 per cent might, under such conditions, appear to be satisfactory. A much larger recovery than 70 per cent is undoubtedly exceptional. The unusually high recovery of 90 per cent and over of the radium present gives the nitric acid method its real value.

TABULATED DATA.

The table following gives the results of the extraction of the first 21 carloads of carnotite ore received at the plant of the National Radium Institute:

Results of extraction of 21 carload lots of carnotite, from ground ore through first and second sulphates.

[All quantities of radium expressed in terms of milligrams of the element.]

Ore.						Sulphates.		First sulphates.								Second sulphates.									
Order of treatment.	Car No.	Weight of moist ore.	Proportion of dry U_3O_8.	Proportion of moisture.	Radium in ore.	Batches.	Number of batches.	Weight of first sulphate.	Weight of average batch.	Radium recovered.	Average radium recovery per batch.	Radium per kilogram.	Proportion of radium recovery.	Weight of ore. Weight of sulphate.	Number of re-treatments.	Weight of second sulphate.	Weight of average batch.	Radium recovered.	Average radium per batch.	Radium per kilogram.	Proportion of radium recovery.	Weight of ore. Weight of sulphates.	Number of retreatments.	Radium returned to plant.	Total radium for recovery.
		Pounds.	*P. ct.*	*P. ct.*	*Mg.*			*Pounds.*	*Lbs.*	*Mg.*	*Mg.*	*Mg.*	*P. ct.*			*Lbs.*	*Lbs.*	*Mg.*	*Mg.*	*Mg.*	*P. ct.*			*Mg.*	*Mg.*
1	4	43,300	2.51	1.52	137.3	1-19	19	287.0	15.1	116.1	6.1	0.90	84.6	151	6	257.0	13.5	3.3	0.17	0.03	2.4	168	15	....	137.3
2	5	41,400	3.04	1.54	158.8	20-37	18	319.2	17.7	141.3	7.85	0.98	89.0	130	4	324.9	18.0	4.5	0.25	0.03	2.8	127	8	....	158.8
3	3	46,280	2.84	1.80	165.4	38-56	19	330.6	17.4	142.9	7.5	0.95	86.4	140	2	218.1	11.5	7.1	0.37	0.07	4.3	212	7	....	165.4
4	2	33,628	3.93	1.20	167.5	57-70	14	212.6	15.2	90.3	6.45	0.94	53.9	158	5	201.0	14.3	3.7	0.26	0.04	2.2	167	5	....	167.5
5	1	43,250	2.66	1.38	145.2	71-87	17	188.7	11.1	56.2	3.3	0.66	38.7	230	0	146.5	8.6	3.3	0.19	0.05	2.3	296	1	....	145.2
6	P-1	61,700	2.27	1.00	177.5	88-110	23	441.2	19.2	142.8	6.2	0.71	80.4	140	4	267.4	10.0	2.3	0.10	0.02	1.3	230	4	....	177.5
7	P-2	80,225	2.69	0.85	274.7	111-142	32	492.9	15.4	244.8	7.65	1.09	89.1	163	3	287.5	9.0	7.3	0.23	0.055	3.0	280	3	....	274.7
8	P-3	74,730	2.79	0.95	264.8	143-171	29	445.4	15.4	242.2	8.35	1.20	89.5	170	1	[a]88.1	6.8	16.4	0.57	0.41	6.0	362	0	5.72	270.5
9	P-4	93,327	2.75	(1.00)	326.3	172-199B	33	470.4	14.3	297.2	9.0	1.39	85.7	198	0	......	......	......	......	......	......	......	....	20.58	346.9
10	P-5	68,000	2.44	(1.00)	211.0	200A-215B	21	307.6	14.6	206.0	9.8	1.47	95.1	221	0	......	......	......	......	......	......	......	....	5.49	216.5
11	P-6	79,200	2.21	(1.00)	221.8	216A-228B	26	567.1	21.8	200.7	7.7	0.77	90.5	140	11	......	......	......	......	......	......	......	....	0.02	221.8
12	P-7	75,800	2.31	1.00	222.4	229A-240B	23	485.5	21.1	181.8	7.9	0.86	81.7	156	8	198.1	8.6	10.7	0.46	0.12	4.8	388	....	....	222.4
13	P-8	72,100	2.73	1.10	250.0	241B-252B	22	518.6	23.6	240.2	10.9	1.02	91.0	139	8	[b]168.	16.8	5.5	0.55	0.07	2.15	429	....	5.57	255.6
14	P-9	82,000	2.36	1.30	244.5	253A-264B	24	473.2	19.7	227.6	9.5	1.06	92.4	174	9	97.6	8.1	5.0	0.41	0.11	2.03	840	....	1.86	246.3
15	P-10	77,000	2.24	1.35	218.0	265A-275B	22	382.9	17.4	211.5	9.6	1.22	95.6	201	5	......	......	......	......	......	......	......	....	3.18	221.2
16	P-11	77,000	2.55	1.25	248.5	276A-286B	22	433.2	19.7	226.3	10.3	1.15	89.9	180	3	......	......	......	......	......	......	......	....	3.13	251.7
17	P-12	82,500	2.53	1.23	264.5	287A-298B	24	421.8	17.5	248.9	10.4	1.30	93.0	196	2	......	......	......	......	......	......	......	....	3.10	267.6
18	P-13	84,000	2.81	1.30	299.0	299A-310B	21	470.6	19.6	290.1	12.2	1.35	96.0	180	3	......	......	......	......	......	......	......	....	3.10	302.1
19	P-14	70,000	2.38	1.18	211.3	311A-320B	20	385.3	19.3	197.1	9.85	1.12	92.5	181	....	......	......	......	......	......	......	......	....	1.60	212.9
20	P-15	82,500	2.96	1.13	309.5	321A-332B	24	534.9	22.3	278.6	11.6	1.15	90.0	154	....	......	......	......	......	......	......	......	....	2.80	312.3
21	P-16	80,000	3.02	2.05	303.2	333A-344B	24	482.3	20.1	275.4	11.4	1.25	90.2	166	....	......	......	......	......	......	......	......	....	2.00	305.1
Total...		1,447,940	......	......	4,821.2	....	480	8,651.0	......	4,258.0	......	......	......	......	74	2,254.2	......	69.1	......	......	......	......	43	58.2	4,879.3
Average		68,950	2.66	1.22	229.6	....	....	412.0	19.6	202.8	8.73	1.08	88.3	1.70	3.5	200	11.4	6.3	0.32	0.07	3.0	3.18	4	....	234.4

[a] 13 batches.

[b] 10 batches.

[c] 12 batches.

DISCUSSION OF TABULATED DATA.

The table shows that with the exception of the ore from two cars, the radium recovered as sulphate has varied from 80.4 to 96 per cent of the radium in the ore with an average of 89.6. If the two cars mentioned are included, the average is 88.3. The average recovery on the last ten carloads treated is 91.5.

In tabulating these results it has been assumed that the radium in the ore is in equilibrium with the uranium, as shown by Lind and Whittemore,[a] and the radium in each carload has been calculated from the uranium oxide content. The radium in the sulphates has always been determined by actual measurement by the emanation method. Results have been accepted only when duplicates gave check results. Although individual sulphate batches were frequently tested, the actual determinations on carload recoveries were made on composites in which the quantity of sulphate used from each batch was proportionate to the total weight of that batch.

During the early part of the work the sulphates were ground and mixed by hand, and a small error in sampling was possible. Later, small ball mills were installed for grinding and thoroughly mixing the sulphates, eliminating the possible error mentioned.

Most of the filtrate from the first sulphate precipitate has carried a little more than 2 per cent of the radium in the ore, as is shown in the column giving the proportion of radium recovery as second sulphates, the filtrate from the second precipitate containing less than 0.1 per cent of the original radium. With four carloads the proportion given was exceeded, the second sulphate from the ore in car P–3 containing 6 per cent of the radium in the ore. The larger part of this was found in three batches and was undoubtedly due to incomplete settling of the first sulphates, a portion of the precipitates being siphoned over and finally appearing with the second sulphate. Indeed, a large part of the average 2 to 2½ per cent loss in the filtrate from the first sulphate is mechanical, not chemical. Efforts are being made to reduce this loss and have already partly succeeded, so well that after the ore in car P–9 had been treated no second sulphates were made.

The ore from cars 1 and 2 gave abnormal results. As regards the ore from car 1, the result can easily be explained, as this ore was part of five cars purchased by the National Radium Institute and had been ground in a ball mill to over 100-mesh fineness instead of being ground to 20 to 30 mesh fineness as is required. Filtration was therefore slow, with a resulting loss of radium. This explanation, however, can not be applied to the ore from car 2, which was readily filtered. Many extraction tests of the ore from this car were made in the laboratory, and only 70 to 75 per cent of the radium could be obtained. Although the amount of sulphate in the ore was fairly high, being 0.21 per cent calculated as sulphuric acid, it was no higher than in the ore from car 4 on which the recovery as sulphate was nearly 85 per cent. The delivery during September, 1915, was 407.5 milligrams, making a total to October 1, 1915, of 2,355 milligrams of radium element.

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[a] Lind, S. C., and Whittemore, C. F., The radium-uranium ratio in carnotites: Tech. Paper 88, Bureau of Mines, 1915, pp. 27–28.

Up to September 1, 1915, 1,947.5 milligrams of radium element had been delivered as high-grade chloride or bromide out of the 4,774 milligrams of radium produced as sulphate. All of this was delivered between February 1 and September 1, 1915, as experimental work on methods of fractionation was not commenced until about December 1, 1914. The grade of the material delivered varied, some containing as much as 87.8 per cent radium. As a rule deliveries were about equally divided between material containing 6 to 15 per cent radium and a higher-grade product containing more than 50 per cent. The lower-grade product is used as a source of emanation for cancer treatment, and the higher-grade product may be used for direct radiation in connection with such work.

A total of 58.2 milligrams of radium from the fractionation process was returned to the plant as barium (radium) chloride. This was low-grade material, the radium content of which was too high to justify its discarding. The large quantity returned in the case of the ore from car P–4 was due to an accumulation from the ore from preceding cars. The total amount of radium discarded in connection with the fractionation of the first 1,646.26 milligrams of element crystallized was 5.13 milligrams, or 0.31 per cent. The radium-barium ratio in this discarded material averaged 25.2 parts per billion.

Except for the discarded liquor mentioned, there are no definite losses that can be indicated quantitatively in refining the radium from the sulphate to the finished product. And yet, there are, of course, small unavoidable losses. The size of these losses will depend largely on the care of the workmen and chemists who do the refining, the personal factor being quite as important as the equipment. In handling and drying the sulphates some small loss through loss of material as dust takes place. In reducing the sulphate with charcoal the evolved gases carry a small amount of sulphate with them. Liquors are occasionally spilt, and "creeping" sometimes takes place in the porcelain and silica vessels in the laboratory. All of these factors can be more or less controlled, and with care the total losses may be kept down to between 1 and 2 per cent. With less careful work they may rise as high as 3 per cent. The loss of one or two crystals of high-grade salt will, of course, have a much greater effect than the careless handling of a large quantity of low-grade material.

The total refining losses at the plant of the National Radium Institute can be only estimated at present. A check on all radium under treatment has been made on more than one occasion, but as nearly 60 determinations were required in each instance the possible total experimental error was much larger than the probable losses. It is believed that the latter have been less than 2 per cent.

RECOVERY OF SODIUM NITRATE.

During the time when crystallization of sodium nitrate from sodium sulphate was necessary, the recovery as usable nitrate was not more than 60 per cent, and sometimes went as low as 50 per cent. With the substitution of nitric for sulphuric acid for a neutralizing agent in the precipitation of the uranium and vanadium, the recovery in nitrate immediately rose to 70 to 75 per cent. More recently the yield has greatly increased, during the months of May, June, and July, 1915, averaging 87.5 per cent, with a minimum of 84.87 per cent and a maximum of 90.04 per cent.

COST OF PRODUCTION.

COST DATA.

During the early stages of the work cost data were kept for all operations, but owing to changes and for other reasons the figures were not subdivided among the several departments in sufficient detail to give the exact data for these departments. Later, this omission was remedied but the departmental figures obtained do not represent an average of the whole operations but rather an average of the results, since the combined plants have been running in connection with the nitric acid plant.

The cost figures include not only expense for labor and materials in connection with the particular operations in question but also the cost of repairs and the actual expense in connection with boiler-room operation, water, electricity, office, laboratory, and superintendence. The figures by departments do not, however, include amortization, insurance, experimental work, cooperation of the Bureau of Mines, and other overhead costs.

The operations have been divided to cover the following items: Leaching, sodium uranate, iron vanadate, sodium nitrate recovery, nitric acid, radium refining, uranium refining, and boiler room.

LEACHING.

Leaching includes operations up to the separation of the barium (radium) sulphate previous to the addition of the acid liquor to an excess of sodium carbonate. The average cost has been $22.62 per ton of ore treated. This item includes the cost of the recovery of the radium as barium (radium) sulphate. If the recovery of uranium and vanadium was not desired, operations could stop at this point. Such a procedure would vary the conditions in connection with the recovery of sodium nitrate; and as the cost of the nitric acid used is based on a definite recovery of sodium nitrate the above figure of $22.62 would be increased if nitric acid or a large proportion of the sodium nitrate for the manufacture of nitric acid had to be purchased.

SODIUM URANATE.

The figure for sodium uranate includes the cost of all operations in connection with the precipitation, filtering, and drying of the uranium as sodium uranate. The average cost has been 31.49 cents per pound of U_3O_3 in the dry sodium uranate.

IRON VANADATE.

The figure for iron vanadate includes the cost of all operations in connection with the precipitation, filtering, and drying of the iron vanadate. The average cost has been 59.1 cents per pound of V_2O_5 in the dry iron vanadate. This part of the work is therefore conducted at an actual loss, but in combination with the sodium-nitrate recovery, which is based on the extraction of the vanadium, is worked at a profit.

SODIUM NITRATE RECOVERY.

The recovery of sodium nitrate involves the evaporation of the sodium-nitrate solution and the crystallization of the nitrate. The cost per pound of sodium nitrate in the recovered salt has averaged 0.3429 cent.

NITRIC ACID.

The cost of nitric acid has varied with the recovery of sodium nitrate, the market price of nitrate used to make up losses, and the cost of repairs. During the past three months (up to Aug. 1, 1915) it has averaged 2.411 cents per pound of 100 per cent acid, and during the preceding two months 2.050 cents per pound on a basis of 80 per cent recovery of the nitrate.

RADIUM REFINING.

Radium refining includes all operations in the plant in the reduction of the barium (radium) sulphates and the fractionation of the chloride liquors up to the point where deliveries are made to the laboratory. The cost has been $2.44 per milligram of radium element delivered to August 1, 1915. At first it was necessary to get the fractionation systems established both at the plant and at the laboratory. Consequently more radium went into the systems than came out. The relative cost of refining at the start, based on the quantity of material delivered, was therefore high. More recently the cost has been reduced to $1.02 per milligram. The cost of refining in the laboratory has been $1.03 per milligram of radium element. This figure includes the salaries of the men engaged in the fractionation work and the cost of chemicals, gas, etc., but does not include the cost of analytical work or supervision or other overhead charges.

EXPENDITURES TO AUGUST 1, 1915.

The expenditures to August 1, 1915, exclusive of those for ore and for Bureau of Mines cooperation, are given below. As already stated, the proper distribution of costs on power, water, etc., was not made to departments during the early experimental part of the work, all such costs being placed under ''plant operation.'' Although this was done later on, as already detailed (pp. 113–115), it has been thought better, in giving the figures below, for the sake of uniformity, to still summarize such costs under ''plant operation.''

Expenditures in plant of National Radium Institute to Aug. 1, 1915.

Construction and equipment:		
Old plant	$21,415.69	
New plant	22,828.65	
Sulphate plant	3,769.31	
Nitric acid plant	4,439.95	
Total charges for construction and equipment		$52,453.60
Operation of plant:		
Old plant (Apr. 1, 1914, to Feb. 1, 1915)	33,250.91	
Combined plants (Feb. 1, 1915, to Aug. 1, 1915)	28,852.90	
Sulphate plant (Oct. 1, 1914, to Aug. 1, 1915)	3,378.01	
Nitric-acid plant (Feb. 2, 1915, to Aug. 1, 1915)	5,973.71	
Chargeable directly to operation		71,455.53
Insurance	1,134.01	
Office expense	897.56	
Laboratory	542.50	
General miscellaneous	2,504.71	
Experimental	919.51	
Chargeable to mines department	2,015.20	
Nitric acid storeroom stock	815.13	
General storeroom stock	3,472.30	
Materials on hand (chemicals, coal, etc.)	3,380.93	
		15,681.85
		139,590.98
Chargeable to mines department	2,015.20	
Nitric acid stock	815.13	
Storeroom stock	3,472.30	
Materials on hand	3,380.93	
		9,683.56
Total		129,907.42

TOTAL COSTS PER GRAM OF RADIUM ELEMENT.

The first ore used in the plant was purchased. This gave an opportunity to test out the process before mining operations were begun. Details of costs of ore mined will be given in a bulletin, being prepared by the Bureau of Mines, on the mining, milling, and concentration of carnotite. These costs cover mining, hauling, freight, grinding, sampling, 70 per cent amortization of equipment, Bureau of Mines cooperation, royalty, and other overhead expenses.

In figuring the total cost of the radium produced, certain overhead expenses, in addition to the cost of the ore and operating costs, that are not included in the operating costs must be charged against the radium. As the plant is in excellent condition and with ordinary repairs, which are taken care of under operating costs, will be perfectly serviceable at least 10 years, an amortization charge for plant and equipment of 20 per cent per annum against each unit from the time it started operation until August 1, 1915, has been made and should be more than ample. The time given to the radium work by the technical men and chemists of the Bureau of Mines has been charged at the full salary rate, a monthly record having been kept of the proportionate amount of his time given by each man. Traveling expenses are also included.

As shown in the table on page 110, 4,258 milligrams of radium element was produced in the form of sulphate from the ore in the first shipments up to and including car P–16, or August 1, 1915. Of this amount, 1,646.56 milligrams of radium element had been delivered, the rest being in the form of untreated sulphate or in process of fractionation. In the table below the cost of refining for delivery these untreated sulphates has been figured at the average refining cost during the last two months considered.

In figuring the cost of the radium, the uranium and vanadium products may be either included or excluded. All the uranium and vanadium has been recovered by the National Radium Institute plant as sodium uranate or uranium oxide and iron vanadate, the whole plant being designed and constructed with this object in view. By subtracting the actual costs connected with the production of the uranium and vanadium compounds from the total cost, a close approximation of the cost of the radium, provided the uranium and vanadium were not recovered, will be obtained, but such a figure will not be exact, as under the changed conditions various factors would enter in, the effects of which can only be estimated. On this basis the average cost of 1 gram of radium element, including the more expensive early treatment, may be determined as follows:

Cost of radium production to Aug. 1, 1915.

Operating costs to Aug. 1:		
Total expenditures	$129,907.42	
Construction and equipment	52,453.60	
		$77,453.82
Cost of ore treated		69,767.99
Amortization of plant and equipment at 20 per cent per annum		9,065.90
Cost of United States Bureau of Mines cooperation (plant department)		13,628.38
Cost of refining 2,611.44 milligrams of radium element (estimated)		5,353.00
		175,269.09
Less costs in connection with the production of the uranium and vanadium compounds		19,947.00
Total cost of 4,258 milligrams of radium element		155,322.09

As already stated, refining losses have almost certainly been less than 2 per cent and probably less than 1 per cent. In order, however, to be on the safe side, an allowance of 3 per cent is made for such losses; 4,258 milligrams less 3 per cent is 4,131 milligrams, which represents the radium finally recovered as high-grade salts. *The average cost of 1 gram of radium element has therefore been $37,599.* It should be remembered that this cost includes the much higher operating costs of the smaller experimental plant and that the first 2 grams of radium extracted cost considerably more per gram than the last 3 grams; also there have been extracted 31,650 pounds of uranium oxide and 11,528 pounds of vanadium oxide. This material has all been contracted for and in part delivered. The returns from its sale will considerably more than cover the cost of its production, and this profit, together with other credits, will ultimately lower by several thousand dollars the cost per gram of radium.

As the price of ore is variable, the question will naturally arise as to the influence of the price of ore on the figures given above. A simple calculation will show at once that the cost of extracting radium, exclusive of the cost of the ore, has been $20,710 per gram. The ore included in the figure of $69,767.99 cited for the cost of ore used in the investigation herein outlined was partly purchased before the war and partly mined by the National Radium Institute at Long Park, Colo. As 723.97 tons was used, the average cost was $96.36 per ton. If the ore had cost $120 per ton, the cost of radium would have been $41,742 per gram, and for every additional amount of $20 per ton above these figures the cost of radium would increase approximately $4,000 per gram.

As it is the hope of the bureau and one of the purposes of this investigation that the miners shall receive a more adequate return for their ore, the figures presented herein will enable anyone interested to determine the approximate cost of radium by the methods outlined under any market price for ore that may prevail.

*

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